EVIDENCE FOR A STEREOSPECIFIC 1,2-ELIMINATION REACTION IN A 1,1-DIAZENE. SYNTHESIS AND DECOMPOSITION OF [N-PHENYL-(*THREO*-(AND *ERYTHRO*)-2-DEUTERIO-1-METHYLPROPYL)AMINO]NITRENE.

Thesis by

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To My Parents

and to Joseph Siefker

ACKNOWLEDGEMENTS

I want to thank my research director, Peter Dervan, for his advice and encouragement during this work. I also want to thank the members of the Dervan group for their help around the lab and through discussions. I am indebted to the staff of the chemistry department and the technicians in the chemistry shops who were always friendly and eager to help. Special thanks go to Chuck Wight and Mary Mandich for running ICR spectra and Jan Owen for typing this thesis. Financial support of this research from the National Science Foundation is acknowledged as well as a graduate fellowship from this same source. Finally I want to thank the friends I've found in Pasadena and the Sierra Nevada for making my stay in California enjoyable. Greetings are extended to anyone who happens to be reading this waiting for the elevator in Millikan.

ABSTRACT

CHAPTER 1:

The mechanism of the formal 1,2-elimination reaction of 1,1-diazenes to alkenes is examined. The syntheses and decomposition of [N-phenyl-(1-methylpropyl)amino]nitrene (**6**), [N-phenyl-(*erythro*-2-deuterio-1-methylpropyl)amino]nitrene (**7**) and [N-phenyl-(*threo*-2-deuterio-1-methylpropyl)amino]nitrene (**8**) are reported. Oxidation of 1-(1-methylpropyl)-1-phenylhydrazine (**9**) with nickel peroxide at 100°C affords 1-butene, *trans*-2-butene, *cis*-2-butene, butane and benzene in ratios of 0.59:0.30:0.097:0.005:1.00. Reaction of the corresponding benzenesulfonamide **10** with base at 100°C affords similar ratios. Oxidation of 1-(*erythro*-2-deuterio-1-methylpropyl)-1-phenylhydrazine (**14**) at 100°C affords 1-butene, *trans*-2-butene (100±2% d_1) and *cis*-2-butene (2.8±2% d_1), and butane in ratios of 0.67:0.30:0.03:0.004. Oxidation of 1-(*threo*-2-deuterio-1-methylpropyl)-1-phenylhydrazine (**20**) at 100°C affords 1-butene, *trans*-2-butene (1.8±2% d_1) and *cis*-2-butene (97.9±2% d_1) and butane in ratios of 0.77:0.11:0.11:0.009. Reaction of the corresponding benzenesulfonamides **15** and **21** with base at 100°C affords similar results. Primary kinetic isotope effects for 2-butene formation from the *erythro* and *threo* 1,1-diazene diastereomers were 3.5 and 3.4, respectively. The 1,1-diazene 1,2-elimination reaction studied here is a stereospecific *cis* elimination process.

CHAPTER 2:

An attempt was made to observe chiral induction in a gas phase IR multiphoton photolysis using a circularly polarized output from a TEA CO_2 laser. The molecule studied was trans-1,2-divinylcyclobutane (**1**) in the gas phase at 0.6 torr. Racemic samples were photolyzed at 977 cm^{-1} (=CHR bending) with 75 focused (0.8-0.9J) pulses. This resulted in about 33% conversion to 1,3-butadiene (**2**), 4-vinylcyclohexene (**3**) and 1.5-cyclooctadiene (**4**). A large number of samples were combined and the **1** (44mg) and **3** (6 mg) were isolated by VPC. Neither showed optical activity.

CHAPTER 3:

The possibility that triazolenitrenes (**2**) are involved in the photodecomposition of s-tetrazines (**1**) is considered. It was found that oxidation of 1-amino-2,5-diphenyl-1,3,4-triazole (**5**) in the presence of tetramethylethylene gave a high yield of triazolenitrene trapping product **6**. Photolysis of 3,6-diphenyl-1,2,4,5-tetrazine (**4**) under these conditions failed to yield the adduct **6**. Unsuccessful attempts were also made to prepare (2,5-di-tert-butyl-1,3,4-triazolidyl)nitrene (**7**) as a persistent species at low temperatures.

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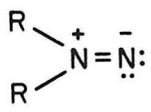
Chapter 1

Evidence for a Stereospecific 1,2-Elimination Reaction in a 1,1-Diazene. Synthesis and Decomposition of [N-Phenyl-(threo-(and erythro)-2-deuterio-1-methylpropyl)amino]nitrene.

1,1-Diazenes (aminonitrenes, N-nitrenes) **1** unlike their more stable 1,2-diazene isomers (azo compounds) **2** are usually not isolated or detected by spectroscopic methods but rather are assumed intermediates on the basis of a substantial body of chemical evidence.[4,5] Recently the syntheses and characterization of persistent 1,1-diazenes have allowed the first direct studies on this reactive species.[6]



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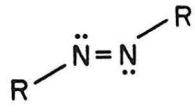
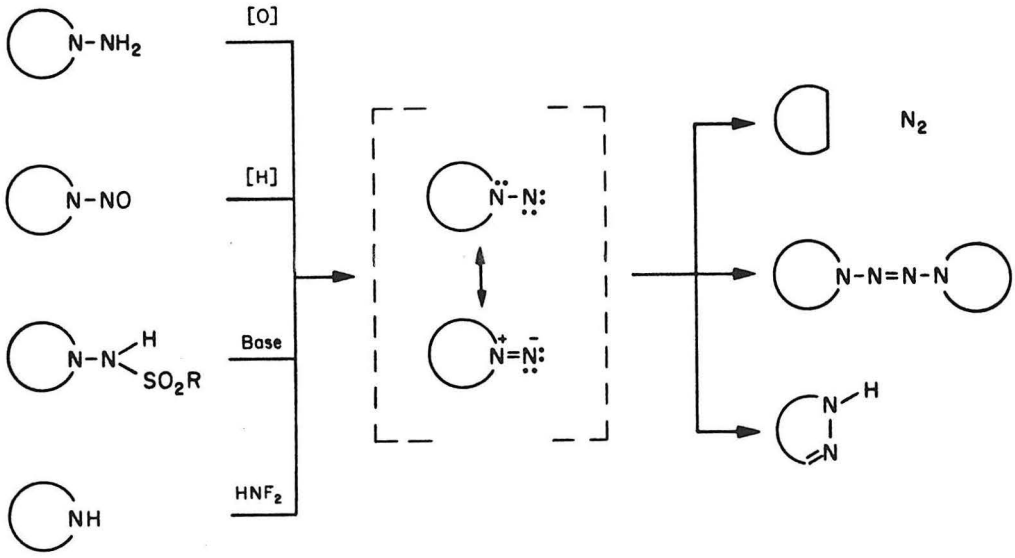


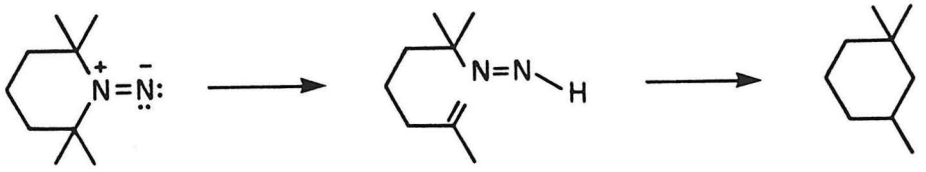
2

There are several methods reported for the generation of 1,1-diazenes, those most versatile being the oxidation of 1,1-disubstituted hydrazines, the reduction of N-nitrosamines, and the base-induced decomposition of 1,1-disubstituted 2-sulfonylhydrazines.[4]

Scheme 1

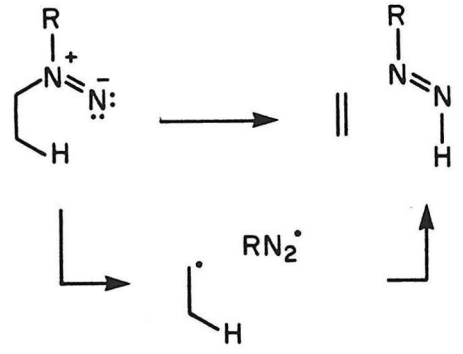


Recent work from our laboratories raised the possibility that in certain cases 1,1-diazenes may undergo a 1,2-elimination reaction to alkene and monosubstituted-1,2-diazene.[6f] Small amounts of 1,1,3-trimethylcyclohexane (**3**) product were observed from the thermal decomposition of N-(2,2,6,6-tetramethylpiperidyl)nitrene (**4**). One mechanistic scheme considered was the radical chain decomposition[7] of a monosubstituted 1,2-diazene **5** derived from a formal 1,2-elimination of 1,1-diazene **4**.[6f]

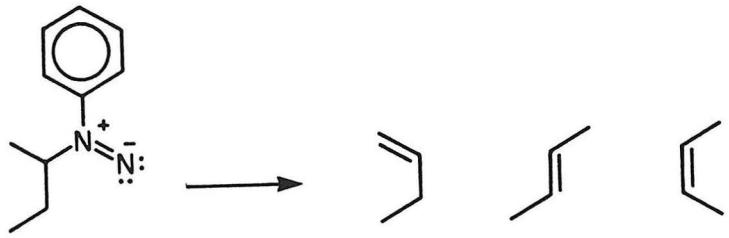


4 **5** **3**

The presumed 1,2-elimination reaction of 1,1-diazenes to alkene could occur stepwise by single bond rupture to an intermediate diazenyl biradical or by a one-step concerted process similar to amine oxides.[8]



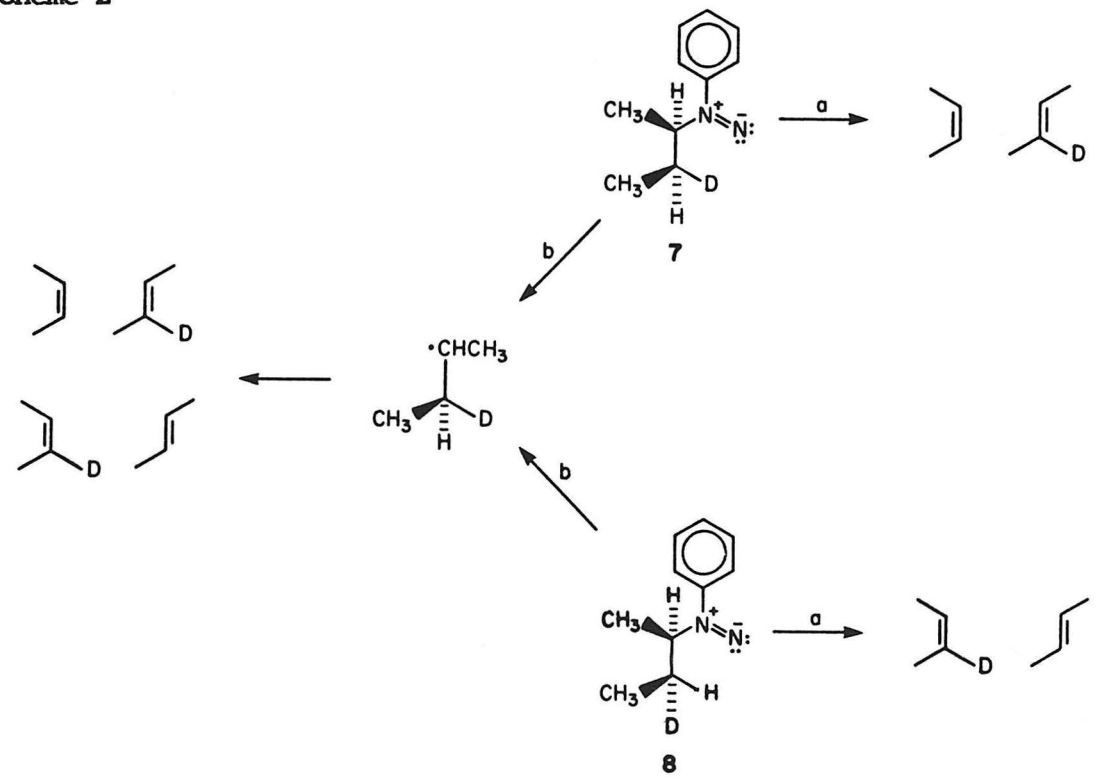
In this paper we report the stereochemical consequences of a 1,1-diazene 1,2-elimination reaction. The test system chosen was [N-phenyl-(1-methylpropyl)amino]nitrene (**6**). Generation of this 1,1-diazene by two different routes affords a high yield of butenes, products of formal 1,2-elimination reactions. We describe here



6

the stereospecific syntheses of precursors for the generation of [N-phenyl-(erythro-2-deuterio-1-methylpropyl)amino]nitrene (**7**) and [N-phenyl-(threo-2-deuterio-1-methylpropyl)amino]nitrene (**8**). Examination of the deuterium label in the trans- and cis-2-butene products should distinguish between a stereospecific cis-1,2-elimination process (path a) and a stepwise pathway via a common 1-methylpropyl radical intermediate (path b).

Scheme 2



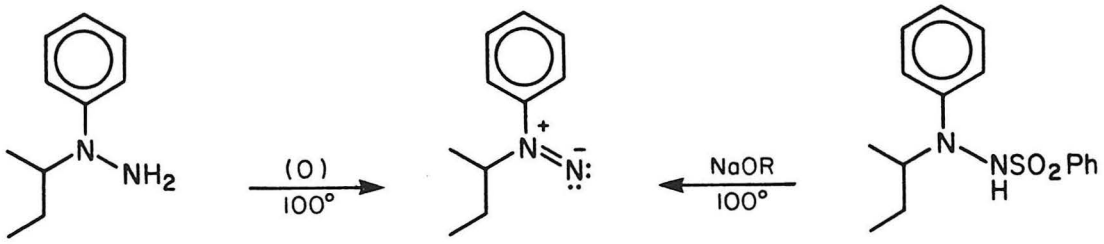
For a stereospecific cis-1,2-elimination process (path a) the erythro disastereomer should afford trans-2-butene-d_1 and

cis-2-butene-d_0. Similarly, the threo diastereomer should afford trans-2-butene-d_0 and cis-2-butene-d_1. The stepwise mechanism (path b) destroys one of the chiral centers that distinguish **7** and **8** and therefore each diastereomeric 1,1-diazene should afford similar ratios of partially deuterated trans- and cis-2-butenes.

Results

Synthesis of 1-(1-Methylpropyl)-1-phenylhydrazine (9) and the Benzenesulfonamide (10). In this study 1,1-diazenes **6**, **7** and **8** were not observed as persistent species, but are presumed transient intermediates. Since the 1,1-diazenes were not directly observed and characterized, they were generated by two different routes in all cases. Product analyses were carried out for comparison from the oxidation reaction of 1-(1-methylpropyl)-1-phenylhydrazine **9** with nickel peroxide (diglyme, 100°C) and decomposition of 2-benzenesulfonamido-1- (1-methylpropyl)-1-phenylhydrazine (**10**) with sodium 2-(2-ethoxyethoxy) ethoxide (diglyme, 100°C).

Scheme 3

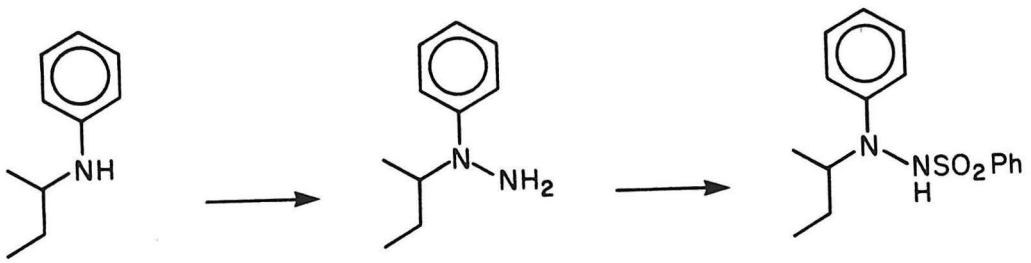


9 **6** **10**

1-(1-Methylpropyl)-1-phenylhydrazine (**9**) and its benzenesulfonamide derivative (**10**) were prepared as outlined in Scheme 4. Reaction of

N-(1-methylpropyl) aniline with freshly prepared O-mesitylenesulfonyl-hydroxylamine afforded 1-(1-methylpropyl)-1-phenylhydrazine (**9**). Subsequent treatment of the alkyl phenylhydrazine **9** with benzenesulfonyl chloride affords the white crystalline 2-benzenesulfonamido-1-(1-methylpropyl)- 1-phenylhydrazine (**10**).

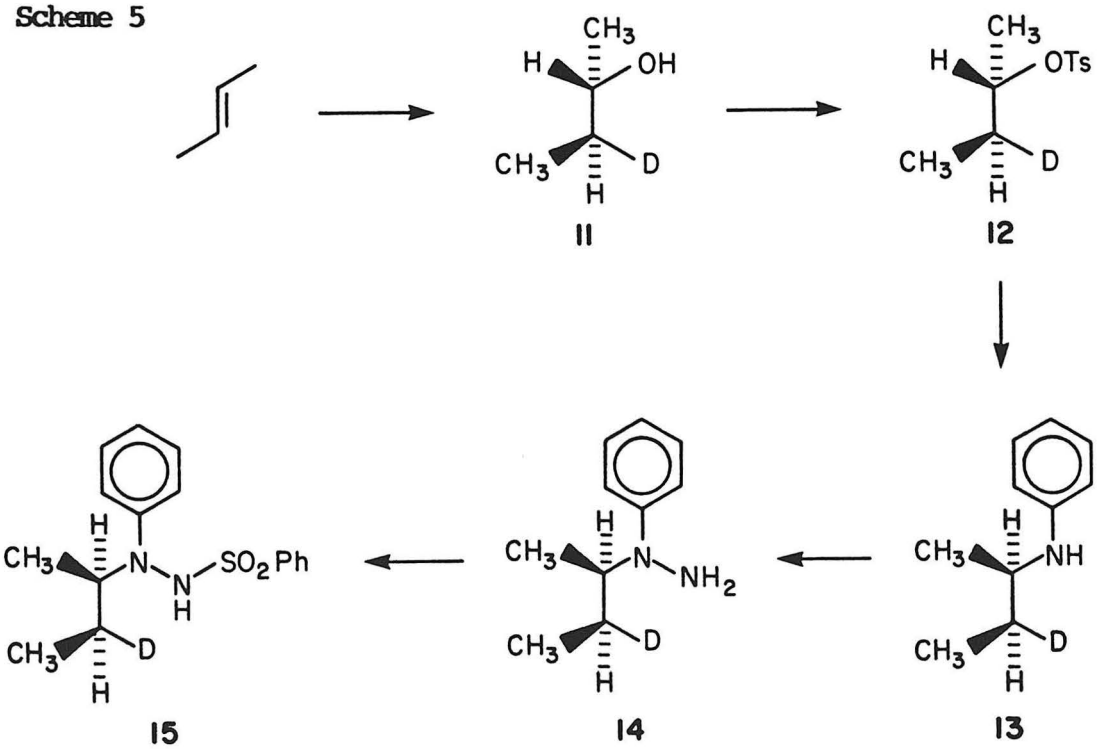
Scheme 4



9 **10**

Synthesis of 1-(Erythro-(and threo)-2-deuterio-1-methylpropyl)-1-phenylhydrazine (14 and 20) and their Benzensulfonamides (15 and 21).

Scheme 5

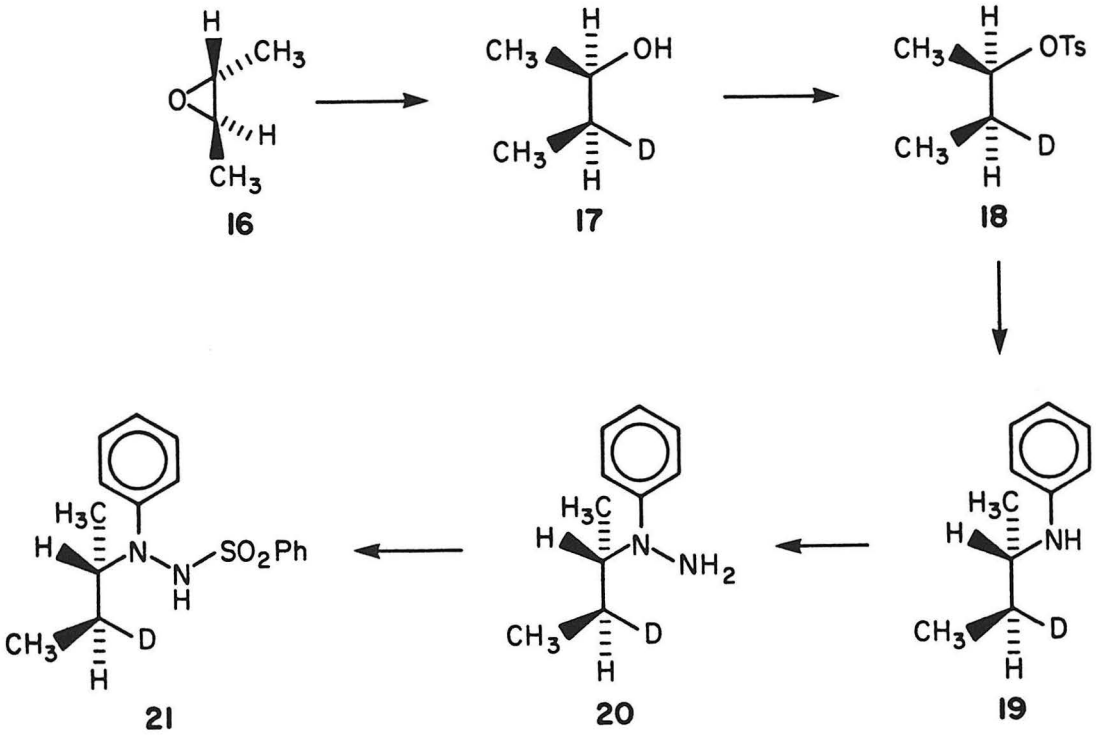


11 **12** **13** **14** **15**

1-(Erythro-2-deuterio-1-methylpropyl)-1-phenylhydrazine (**14**) and its benzenesulfonamide derivative (**15**) were prepared from trans-2-butene by known synthetic methodology as outlined in Scheme 5.

Similarly, 1-(threo-2-deuterio-1-methylpropyl)-1-phenylhydrazine (**20**) and its benzenesulfonamide derivative (**21**) were prepared from trans-2-butene as outlined in Scheme 6.

Scheme 6



The diastereomeric purities of the materials from Schemes 5 and 6 were shown to be >98% from proton decoupled high field (76.7 MHz) ^{2}H NMR of the diasteromeric amines **13** and **19**. The erythro and threo amine diastereomers, **13** and **19**, give singlets at 1.49 and 1.62 ppm respectively (Figure 1).

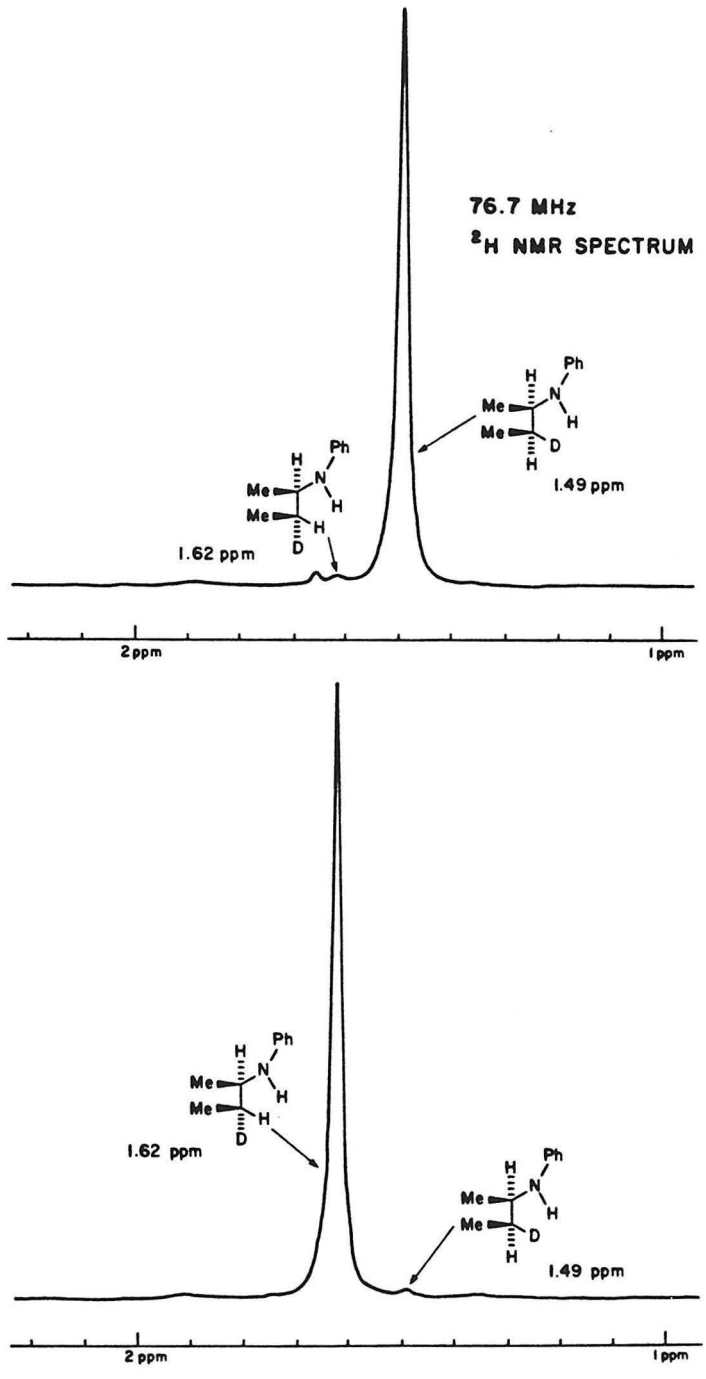
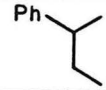
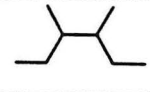


Figure 1. ^{2}H NMR spectrum of amines **13** and **19**.

Generation and Decomposition of 1,1-Diazenes 6-8

The hydrocarbon products from the generation and decomposition of 1,1-diazene **6** by two routes were analyzed by analytical VPC and are shown in Table 1.

Table 1. Hydrocarbon Product Ratios[a] from Generation and Thermolysis of **6** at 100°C.[b]

Precursor							
9	59.3	30.4	9.7	0.5	100	<0.5	<0.3
10	58.8	30.6	9.6	1.1	75	<0.5	<0.3

[a]Molar ratios. [b]Absolute yield of C_4 hydrocarbon was typically 60% by the benzensulfonamide/base route and 13% by the hydrazine/peroxide route.

It can be seen that the formal 1,2-elimination reaction is the major pathway for the decomposition of **6**. The presence of small amounts of butane indicates that the stepwise process is probably occurring to some extent. The mechanism for the generation of the butenes cannot, however, be determined from these data. The presence of a high yield of benzene is consistent with either mechanism.

The relative C_4 hydrocarbon ratios and the deuterium content for the butenes resulting from the thermolysis of **7** and **8** are presented in Tables **2** and **3**. The hydrocarbon ratios were measured by analytical VPC against an internal standard. The hydrocarbon products were separated and isolated by preparative VPC for analysis of deuterium content by ion cyclotron resonance spectroscopy (ICR). Oxidation of

1-(erythro-2-deuterio-1-methylpropyl)- 1-phenylhydrazine (**14**) at 100° affords trans-2-butene (100±2% d_1) and cis-2-butene (2.8±2% d_1). Oxidation of 1-(threo-2-deuterio-1-methylpropyl)- 1-phenylhydrazine (**20**) at 100° affords trans-2-butene (1.8±2% d_1) and cis-2-butene (97.9±2% d_1). Reaction of the corresponding benzenesulfonamides **15** and **21** with base at 100° affords similar results (Table 3).

Table 2. Hydrocarbon Ratios from Decomposition of **7** and **8** at 100°C[a]

Precursor				
erythro				
14	66.8	29.8	3.0	0.4
15	65.5	30.1	3.1	1.2
threo				
20	76.7	11.3	11.1	0.9
21	75.7	11.6	11.3	1.4

[a]Molar ratios

Table 3. Deuterium Content of 2-Butenes from Decomposition of **7** and **8** at 100°C[a]

Precursor	trans	cis
erythro		
14	100±2	2.8±2
15	99.9±1	3.9±1
threo		
20	1.8±2	97.9±2
21	1.9±2	98.7±2

[a]See Experimental Section.

Discussion

The fact that the butene ratios and deuterium content for the oxidative and benzenesulfonamide decomposition routes match so closely supports the notion that both routes are going through a common intermediate, presumably the 1,1-diazene. From the data presented in Tables 2 and 3 the thermal decomposition of [N-phenyl-(erythro-2-deuterio-1-methylpropyl)amino]nitrene (**7**) and [N-phenyl-(threo-2-deuterio-1-methylpropyl)amino]nitrene (**8**) to 2-butene is predominantly a stereospecific cis-1,2-elimination reaction. The crossover deuterium content in cis-2-butene from erythro **7** and in trans-2-butene from threo **8** may simply be a reflection of the diastereomeric purities of the starting materials (>98%). Importantly, the crossover deuterium content sets an upper limit of a few percent for the stepwise 1,2-elimination process.

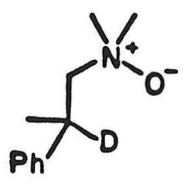
The data in Tables 1 and 2 permit the calculation of deuterium isotope effects for the elimination reactions of **7** and **8**. From the undeuterated benzensulfonamide **10**, the ratios of 1-butene:trans-2-butene:cis-2-butene products are 1.00:0.520:0.163 (Table 1). From the erythro series **15**, these ratios change to 1.00:0.460:0.047. Assuming the rate of 1-butene formation does not change the major observation is that for the erythro deuterated diastereomer **7** there is a decrease in cis-2-butene formation by a factor of 3.5, a primary deuterium isotope effect. In addition, a small decrease in trans-2-butene formation occurs, which allows calculation of a secondary deuterium isotope effect for the 1,2-elimination reaction, k_H/k_D=1.13. Similarly, from the threo precursor **21**, the ratios of 1-butene: trans-2-butene:cis-2-butene

products are 1.00:0.153:0.149 (Table I). In this case the major observation from the threo deuterated diastereomer **8** is a decrease in trans-2-butene formation by a factor of 3.4, a primary deuterium isotope effect, and a small decrease in cis-2-butene production, affording the secondary deuterium isotope effect, k_H/k_D=1.09. The primary deuterium kinetic isotope effects for several Cope elimination reactions believed to be concerted are in the same range and are shown for comparison (Table 4).[8]

Table 4. Primary Kinetic Isotope Effects for 1,2-Elimination Reactions of 1,1-Diazenes **7** and **8** and Selected Amine Oxides.

Precursor	Temp.	k_H/k_D	Reference
Diazene **7**	100°C	3.5	a,b
Diazene **8**	100°C	3.4	a,b
23	52°C	3.0	8d
24	110-120°C	3.5	8c
25	90/110°C	2.2	8e

[a]This work. [b]These numbers were calculated from the benzensulfonamide data by assuming that the rate constants for formation of 1-butene are the same for 1,1-diazene **6-8** at 100°C.



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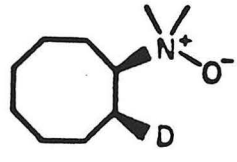

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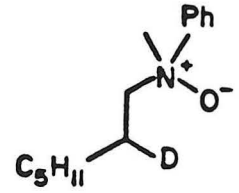

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Experimental Section

Melting points were determined by using a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 infrared spectrophotometer. Proton NMR spectra were obtained on a Varian Associates EM-390 spectrometer. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane in δ units and coupling constants are in Hertz (Hz). NMR data are reported in this order: chemical shift; multiplicity, s=singlet, d=doublet, t=triplet, m=multiplet; number of protons; coupling constants. Deuterium NMR spectra were run on a Bruker WM-500 spectrometer. Peak positions are given in ppm δ units. $CDCl_3$ was used as internal standard and assigned the value of 7.25 ppm. Carbon NMR spectra were run on a Jeol FX-90Q. For capillary vapor phase chromatography (VPC) a Hewlett-Packard 5700A gas chromatograph equipped with a Hewlett-Packard 18704A inlet splitter and a flame ionization detector was used. Hydrogen was employed as the carrier gas and the makeup gas was nitrogen. Packed column analytical VPC was done using a Hewlett-Packard 5720A gas chromatograph equipped with a flame ionization detector and nitrogen carrier gas. This instrument was used with 0.125 in. packed stainless steel columns. All quantitative VPC analysis was accomplished using a Hewlett-Packard 3390A electronic integrator. VPC response factors for normal aliphatic hydrocarbons were assumed to be 1.00 relative to butadiene. Quantitative analyses of other compounds were corrected for detector response. For preparative VPC a Varian 920 instrument equipped with a thermal conductivity detector and helium carrier gas was used. This instrument was used with 0.25 in. glass or 0.375 in. aluminum packed

columns. VPC columns used are listed below. The identities of butane and benzene were verified by coinjection techniques. Isotope compositions of the butenes were determined using an ion cyclotron resonance spectrometer operated with an electron impact energy of 9 or 10 eV to provide ionization with negligible fragmentation. Gas pressures were measured with an MKS type 221 capacitance manometer. UV spectra were recorded using a Beckman Model 25 spectrophotometer.

VPC Columns

Designation	Description
Carbowax 20M capillary	50 Meter 0.31 mm ID fused silica Carbowax 20M capillary
Pennwalt	6 ft.x1/4 in. glass; 28% Pennwalt 223 80/100 Chrom R
$\beta\beta$	20 ft.x1/8 in. stainless steel; 15% β,β'-oxydipropionitrile on 100/120 Chrom P-NAW
DMS	20 ft.x3/8 in. aluminum; 25% 2,4-dimethylsulfolane on 80/100 Chrom P-NAW
Carbowax 20M	10 ft.x3/8 in. aluminum; 25% Carbowax 20M on 60/80 Chrom W-AW-DMCS

Dichloromethane was dried by distillation from calcium hydride.

Triethylamine and pyridine were dried over 4A molecular sieves. Benzenesulfonyl chloride was distilled under an argon atmosphere. The procedure described by Pelletier was used for the purification of p-toluenesulfonyl chloride.[9] Aniline was distilled from zinc dust at reduced pressure then dried over 4A molecular sieves. N-(1-methylpropyl)aniline was distilled from zinc dust at reduced pressure. Diglyme was fractionally distilled at reduced pressure then distilled from calcium hydride at reduced pressure just prior to use. Nickel peroxide was prepared then activated with sodium hypochlorite according to the procedure of Nakagawa et al.[10] Sodium 2-(2-ethoxyethoxy)ethoxide was prepared by dissolving sodium metal in 2-(2-ethoxyethoxy)ethanol. 3,4-Dimethylhexane was obtained from Albany International and shown to be about an equal mixture of the two diastereomers by ^{13}C NMR.[11] Butadiene used as a VPC standard was purified by preparative VPC (DMS room temperature). The p-xylene used as a VPC standard was also purified by preparative VPC (Carbowax 20M). Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. Reactions were carried out under a positive pressure of argon.

O-Mesitylenesulfonylhydroxylamine. This reagent was prepared fresh for each amination using the procedure described by Tamura et al.[12] NMR ($CDCl_3$) δ 7.0 (s, 2H), 4.7 variable (s broad, 2-3), 2.6 (s, 6H), 2.2 (s, 3H).

1-(1-Methylpropyl)-1-Phenylhydrazine (9). A 500 mL round bottom flask was charged with 13.3g (0.089 mole) of N-(1-methylpropyl)aniline and 120 mL of dichloromethane. This mixture was cooled to 0°C then a solution of 19.8g (0.092 mole) of O-mesitylenesulfonylhydroxylamine in

120 mL dichloromethane was added dropwise with stirring. After addition was complete stirring was continued for 3 minutes. The cooling bath was then removed and stirring was continued for 20 minutes. The reaction mixture was combined with 25% aqueous sodium hydroxide and ether, then filtered through Celite. The organic phase was extracted several times with 3 N HCl. The acidic aqueous phase was cooled with ice and made strongly basic by adding 25% sodium hydroxide solution. This was then extracted several times with ether. The organic phase was dried (Na_2SO_4) and the ether was removed by distillation. Fractional distillation at reduced pressure yielded 2.7g (18%) of 1-(1-methylpropyl)-1-phenylhydrazine (**9**) b.p. 69-77°C (0.3 torr). This was further purified by preparative VPC (Pennwalt, 180°C). IR (film) 3360, 2980, 1605, 1500, 1460, 1385, 1290, 1260, 1160, 1000, 875, 760, 700 cm^{-1}; NMR ($CDCl_3$) δ 6.6-7.4 (m, 5), 3.5-3.9 (m, 1), 3.2 (s, broad, 2), 1.2-1.9 (m, 2), 0.8-1.1 (m, 6). Anal. Calcd. for $C_{10}H_{16}N_2$: C 73.13; H, 9.82; N, 17.05. Found: C, 72.97; H, 10.00; N, 16.92.

2-Benzenesulfonamido-1-(1-Methylpropyl)-1-Phenylhydrazine (10). A flask was charged with 8 mL dry dichloromethane, 652 mg (4.0 m mole) of 1-(1-methylpropyl)-1-phenylhydrazine (**9**) and 436 mg (4.3 m mole) of dry triethylamine. This mixture was cooled to -20°C and 700 mg (4.0 m mole) of freshly distilled benzenesulfonyl chloride was added dropwise with stirring. Stirring was continued for 15 minutes then the mixture was warmed to 0°C and stored at this temperature for 2 days. The mixture was then diluted with 25 ml of dichloromethane, washed 3 times with water, once with 10% HCl then once with saturated sodium bicarbonate. The organic phase was then dried (Na_2SO_4) and

concentrated affording a brown oil. This was then purified by preparative thin layer chromatography (silica gel/dichloromethane). The resulting product was dissolved in dichloromethane/petroleum ether, treated with Norit SG, then filtered. This solution was then concentrated and the resulting oil allowed to solidify at -20°C, then recrystallized from petroleum ether to yield 325 mg (27%) of white crystalline benzensulfonamide **10**. M.P. 81-81.5°C; IR (CCl_4) 3250, 2980, 1600, 1495, 1450, 1345, 1170, 1095 cm^{-1}; NMR ($CDCl_3$) δ 6.7-7.9 (m, 10) 6.5 variable (s, 1), 3.2-3.5 (m, 1), 1.1-1.8 (m, 2), 0.75-1.05 (m, 6). Anal. Calcd. for $C_{16}H_{20}N_2SO_2$: C, 63.13; H, 6.62; N, 9.20. Found: C, 63.38; H, 6.80; N, 9.25.

threo-2-Butanol-3-d_1. This compound was prepared from trans-2-butene using the procedure of Kabalka and Bowman.[13] NMR ($CDCl_3$) δ 3.5-3.85 (m, broad, 1), 2.0 (s, broad, 1), 1.2-1.6 (m, 1), 1.15 (d, 3, J=7Hz), 0.9 (d, 3, J=7Hz).

threo-2-Butanol-3-d_1 Tosylate. A 1L flask was charged with 27.3g (0.36 moles) of threo-2-butanol-3-d_1 and 525 mL dry pyridine. This mixture was cooled to 0°C and 137g (0.72 moles) of p-toluenesulfonyl chloride was added with stirring. Stirring was continued until all material had dissolved. The mixture was allowed to stand at 0°C for 2 days, then poured into 3.3L of ice water and extracted several times with ether. The combined organic phase was washed successively with cold 1:1 hydrochloric acid and water. The solution was dried (K_2CO_3/Na_2SO_4), concentrated, taken up in a minimum volume of petroleum ether, treated with Norit SG, filtered, then slowly cooled to -78°C. The petroleum ether was then transferred from the product. Warming to room temperature yielded 63.5g (77%) of a colorless oil.

IR (film) 2995, 1367, 1193, 1180, 910 cm^{-1}; NMR ($CDCl_3$) δ 7.8 (d, 2, J=8Hz), 7.3 (d, 2, J=8Hz), 4.35-4.7 (m, 1), 2.4 (s, 3), 1.3-1.65 (m, 1), 1.2 (d, 3, J=6Hz), 0.8 (d, 3, J=7Hz).

N-(erythro-2-Deuterio-1-Methylpropyl)Aniline (13). A flask was charged with 350 mL dry ether and 15.6g (0.17 mole) of aniline. This mixture was cooled to -78°C then 0.17 moles of methyllithium-lithium bromide complex in ether was added dropwise with stirring. After 0.5 hours the cold bath was removed and stirring was continued for 1 hour. The mixture was cooled to 0°C and 24.0g (0.11 mole) of threo-2-butanol-3-d_1 tosylate was added dropwise with stirring. The mixture was warmed to room temperature and stirred for 2 days. Water and dichloromethane were added, the mixture was filtered through Celite, and extracted three times with 3 N hydrochloric acid. The combined aqueous phase was made strongly basic with 25% sodium hydroxide solution then extracted with ether. The organic solution was dried (Na_2SO_4) and concentrated. The product was isolated by fractional distillation at reduced pressure yielding 8.9g (56%). IR (film) 3420, 2980, 1610, 1510, 1320, 755, 695 cm^{-1}; NMR ($CDCl_3$) δ 7.0-7.25 (m, 2), 6.45-6.7 (m, 3), 3.15-3.5 (m, broad, 2), 1.35-1.7 (m, 1), 1.1 (d, 3, J=7Hz), 0.9 (d, 3, J=8Hz). Deuterium NMR ($CHCl_3$) δ 1.49 (s).

1-(erythro-2-Deuterio-1-Methylpropyl)-1-Phenylhydrazine (14). This compound was prepared from N-(erythro-2-deuterio--1-methylpropyl)aniline (**13**) using the procedure described for 1-(1-methylpropyl)-1-phenylhydrazine (**9**). NMR ($CDCl_3$) δ 6.6-7.3 (m, 5), 3.5-3.85 (m, 1), 3.1 (broad s, 2), 1.4-1.8 (m, 1), 1.05 (d, 3, J=6Hz), 0.9 (d, 3, J=7Hz).

2-Benzenesulfonamido-1-(erythro-2-Deuterio-1-Methylpropyl)-1-Phenylhydrazine (15). This compound was prepared from 1-(erythro-2-deuterio-1-methylpropyl)-1-phenylhydrazine (**14**) using the procedure described for the preparation of 2-benzenesulfonamido-1-(1-methylpropyl)-1-phenylhydrazine (**10**). NMR ($CDCl_3$) δ 6.6-7.9 (m, 10), 6.5 (s, 1), 3.15-3.5 (m, 1), 1.4-1.8 (m, 1), 1.0 (d, 3, J=7Hz), 0.9 (d, 3, J=8Hz).

erythro-2-Butanol-3-d_1. This compound was prepared from trans-2-butene using the procedure of Jackman and Bowman.[14] NMR ($CDCl_3$)δ3.45-3.85 (broad m, 1), 2.4 (broad d, 1, J=3Hz), 1.25-1.65 (m, 1), 1.15 (d, 3, J=6Hz), 0.9 (d, 3, J=7Hz).

erythro-2-Butanol-3-d_1 Tosylate. This compound was prepared from erythro-2-butanol-3-d_1 using the procedure described for threo-2-butanol-3-d_1 tosylate. IR (film) 2990, 1360, 1190, 1180, 910 cm^{-1}; NMR ($CDCl_3$) δ 7.75 (d, 2, J=8Hz), 7.3 (d, 2, J=8Hz), 4.35-4.7 (m, 1), 2.4 (s, 3), 1.4-1.75 (m, 1), 1.2 (d, 3, J=6Hz), 0.8 (d, 3, J=8).

N-(threo-2-Deuterio-1-Methylpropyl)aniline (19). This compound was prepared from erythro-2-butanol-3-d_1 tosylate using the procedure described for N-(erythro-2-deuterio-1-methylpropyl)aniline (**13**). IR (film) 3410, 2980, 1610, 1510, 1320, 750, 695 cm^{-1}; NMR ($CDCl_3$) δ 7.0-7.3 (m, 2), 6.4-6.75 (m, 3), 3.15-3.5 (m, 2), 1.2-1.6 (m, 1), 1.1 (d, 3, J=6Hz), 0.9 (d, 3, J=8Hz). Deuterium NMR ($CHCl_3$) δ 1.62 (s).

1-(threo-2-Deuterio-1-Methylpropyl)-1-Phenylhydrazine (20). This compound was prepared from N-(threo-2-deuterio-1-methylpropyl)aniline (**19**) using the procedure described for 1-(1-methylpropyl)-1-phenylhydrazine (**9**). NMR ($CDCl_3$) δ 6.5-7.3 (m, 5), 3.5-3.9 (m, 1), 3.1 (broad s, 2), 1.2-1.55 (m, 1), 1.05 (d, 3,

J=6Hz), 0.85 (d, 3, J=8Hz).

2-Benzenesulfonamido-1-(threo-2-Deuterio-1-Methylpropyl)-1-Phenylhydrazine (21). This compound was prepared from 1-(threo-2-deuterio-1-methylpropyl)-1-phenylhydrazine (**20**) using the procedure described for 2-benzenesulfonamido-1-(1-methylpropyl)-1-phenylhydrazine (**10**). NMR ($CDCl_3$) δ 6.6-7.8 (m, 10), 6.3 (s, 1), 3.1-3.5 (m, 1), 1.05-1.4 (m, 1), 1.0 (d, 3, J=7Hz), 0.9 (d, 3, J=8Hz).

1,4 Di(1-Methylpropyl)-1,4 Diphenyl-2-Tetrazene (22). A round bottom flask was charged with 25 mL diethyl ether, 1.8g of nickel peroxide (equivalent to 15 m mole· OH) and a magnetic stir bar. The mixture was cooled to 0°C and a solution of 318 mg (1.9 m mole) of 1-(1-methylpropyl)-1-phenylhydrazine (**9**) in 2 mL diethyl ether was added over about 15 seconds. Stirring was continued for 1 hour at 0°C then 1 hour at room temperature. The mixture was filtered and the solvent removed at reduced pressure to yield a brown oil. This was crystallized by dissolving in a small volume of ethanol then cooling to -78°C. This yielded 50 mg (16%) of a light yellow solid. This was recrystallized to afford a white solid. M.P. 35.5-36°C; IR (CCl_4) 2980, 1600, 1495, 1060 cm^{-1}; NMR ($CDCl_3$) δ 6.8-7.45 (m, 10), 4.15-4.5 (m, 2), 1.4-2.2 (m, 4), 1.3 (d, 6, J=7Hz), 0.9 (t, 6, J=7Hz). Anal. Calcd. for $C_{20}H_{28}N_4$: C, 74.03; H, 8.70; N, 17.27. Found: C, 74.15; H, 8.70; N, 17.23; UV (cyclohexane) 337 nm (ϵ19000), 305 nm shoulder (ϵ 12000), 257 nm (ϵ9400).

Generation and Decomposition of 1,1-Diazenes 6-8 by the Benzensulfonamide/Base Route. In a typical run 150-300 mg of the deuterium labeled benzenesulfonamide **15** or **21** was dissolved in 1.5- 4 mL of dry diglyme and placed in one side of a 2 fingered sealable

reaction cell. The other finger was charged with 0.8 equivalents of sodium 2-(2-ethoxyethoxy)ethoxide in 2-(2-ethoxyethoxy)ethanol and 2-4 mL diglyme. The reaction cell was degassed and sealed under vacuum. After heating the cell to 100°C in an oil bath, the base and benzenesulfonamide solutions were mixed and heating at 100°C was continued for 3-4.5 hours. The reaction mixture was frozen with liquid nitrogen, the reaction cell broken open and immediately connected to a vacuum manifold by means of a standard taper joint. The reaction mixture was vacuum transferred to another tube and after warming to -78°C the solution was analyzed for C_1-C_4 hydrocarbons by VPC ($\beta\beta$,0°C). For yield determination 1,3-butadiene was used as internal standard. No C_1-C_3 hydrocarbons were observed in these reactions. The absolute yield of C_4 hydrocarbons was typically 60%. The mixture was connected to the vacuum line and the volatile hydrocarbons were isolated by repeatedly exposing the reaction mixture to a large volume, isolating the reaction mixture and condensing the contents into a new tube. Finally, the volatile hydrocarbons were frozen with 0.25-0.3 mL of 2,2,4-trimethylpentane on the vacuum line. This mixture was removed from the line, warmed to -78°C and injected into a preparative VPC by means of a chilled syringe. The 1-butene, trans-2-butene and cis-2-butene were separated and isolated by preparative VPC (DMS, 25°). The isolated hydrocarbons were analyzed for purity by condensing small portions of the samples with 2,2,4-trimethylpentane on a vacuum line for VPC analysis ($\beta\beta$, 0°C). The isolated butene samples were dried by transferring them on a vacuum line from a tube at -78°C to one cooled with liquid nitrogen. The dry purified butene samples were then analyzed for deuterium

content by ICR. The unlabeled 1,1-diazene (**6**) was generated in a similar manner on a smaller scale. Benzene, 3,4-dimethylhexane and (1-methylpropyl)benzene products were analyzed by analytical VPC (Carbowax 20 M Capillary, 100°C).

Generation and Decomposition of 1,1-Diazenes 6-8 by the Alkyl-Phenylhydrazine/Oxidation Route. In a typical run 300-400 mg of the deuterium labeled 1-(1-methylpropyl)-1-phenylhydrazine **14** or **20** was dissolved in 25 mL diglyme and placed in one chamber of a sealable reaction cell with 2 chambers separated by a Teflon vacuum valve. The other chamber was charged with a 10 fold excess of nickel peroxide in 25 mL diglyme. The reaction cell was degassed and sealed under vacuum. After heating to 100°C in an oil bath, the valve separating the chambers was opened and the solution of labeled 1-(1-methylpropyl)-1-phenylhydrazine was gradually mixed with the nickel peroxide over a 15 minute period while heating was continued. After cooling, the mixture was analyzed and separated as described above for the benzenesulfonamide route. The absolute yield of C_4 hydrocarbons ranged 5-13%. No butadiene or methane was generated in these reactions. The unlabeled 1,1-diazene **6** was generated in a similar manner from **9** on a smaller scale. Benzene, 3,4-dimethylhexane and (1-methylpropyl)benzene products were analyzed by analytical VPC (Carbowax 20M Capillary, 100°C). Generation of labeled and unlabeled [N-phenyl-(1-methylpropyl)amino]nitrene by this route also gave trace variable amounts of C_2 and C_3 hydrocarbons. The ranges observed for C_2 and C_3 hydrocarbons are given below as molar percent of the C_2-C_4 mixture: propene, $\leq$0.4%; propane, $\leq$0.2%; ethene, 0.4-5.7% ethane, $\leq$1.0%. Heating diglyme and nickel peroxide together at 100°C in the

absence of **9** afforded no C_1-C_4 hydrocarbons.

Deuterium Analyses.[15] The butenes that were isolated by VPC from decomposition of 1,1-diazenes **7** and **8** had the following isomeric purities: 1-butene > 99.99%; trans-2-butene > 99.0%; cis-2-butene > 98.5%. The isotopic compositions of the 1-butene samples were determined by dividing the ICR peak heights by respective peak masses. For trans-2-butene and cis-2-butene,corrections were applied where needed for the presence of the ^{13}C peak in the ICR. For trans-2-butene and cis-2-butene analyses, corrections were made for trace contamination by other butene isomers. These corrections were based on the concentrations, labeling and relative ionization cross sections of the contaminants. The contributions of non-deuterated 1,1-diazene precursor to the trans-2-butene and cis-2-butene data were then determined. The percentage of deuterated material in the 1-butene sample for a given run was recorded and taken as a measure of the isotopic purity of the 1,1-diazene (typically 98% d_1). From this value, the butene product ratios for decomposition of **7** and **8**, and the butene product ratios for the decomposition of unlabeled **6**, it was possible to determine the unlabeled 1,1-diazene contribution to the m/e 56 peak of the trans and cis-2-butene ICR spectra. These contributions were subtracted from the ICR data before these data were used to calculate the isotopic compositions of the 2-butenes. The data in table 8 are corrected for the presence of wrong butene isomers but not adjusted to correspond to 100% D starting material. The data in table 3 are corrected to correspond to 100% D starting material and 100% isomerically pure butene products.

Table 8. Isotopic Compositions of Butenes from Thermolysis of (**7**) and (**8**) at 100°C.

Precursor			
15	98.2% D	97.9% D	3.6% D
14	98.8% D	98.6% D	2.6% D
21	98.5% D	1.8% D	97.1% D
20	98.7% D	1.8% D	96.4% D

Thermolysis of Tetrazene 22.

1,4-Di-(1-methylpropyl)-1,4-diphenyl- 2-tetrazene (**22**) was heated for 5.5 hours at 100°C as a degassed solution in diglyme. This resulted in the formation of <0.1% C_1-C_4 hydrocarbons.

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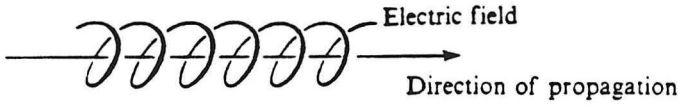
Chapter 2

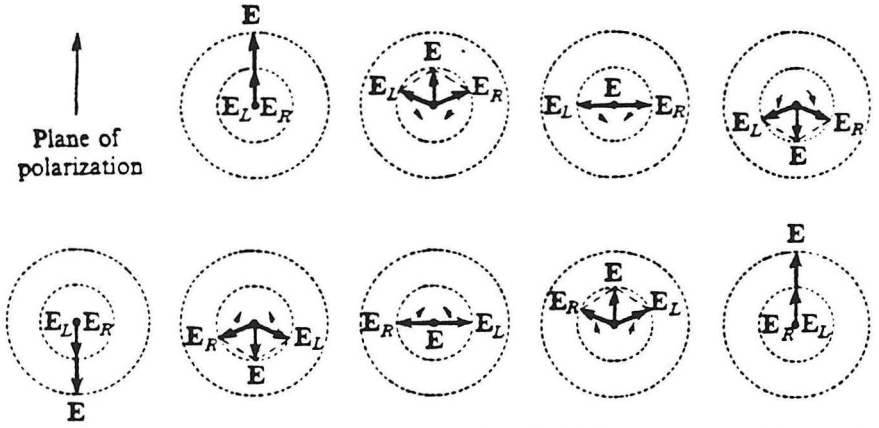
Attempted Chiral Induction via Multiphoton Infrared Photolysis.

Dissymmetric molecules (i.e., those lacking an alternating axis of symmetry) are known to exhibit several unique and interesting optical properties. When plane polarized light is passed through a solution containing a dissymmetric species (and less than an equivalent amount of its mirror image) the plane of polarization of the radiation is rotated. This property is understood by viewing[1] the plane polarized light as a superposition of right and left circularly polarized components of equal intensity. This is indicated in figures[2] 1 and 2.



Right circularly polarized light wave.

Figure 1



Right and left circularly polarized electric field vectors combining to give plane-polarized field vector. (*From C. Djerassi, "Optical Rotatory Dispersion," copyright, 1960, McGraw-Hill Book Company, Inc.*)

Figure 2

In a dissymmetric medium,[3] the index of refraction for left circularly polarized (LCP) light n_L will be different than that for

right circularly polarized (RCP) light n_R. In other words, the speed of LCP light will differ from that of RCP light as they pass through the medium. The relative phases of RCP and LCP light will be changed after passing through the sample, as a result of this velocity difference. If the light entering the sample is plane polarized, this will result in a rotation of the plane of polarization, relative to its original orientation.

Another fascinating property related[4] to this manifests itself in the absorption of light by the molecule. The extinction coefficient for RCP light ϵ_R will be different from that for LCP light ϵ_L, when the absorbing species is a dissymmetric molecule. This phenomenon is known as circular dichroism (CD). The value of ϵ_R for a dissymmetric species will be equal to ϵ_L for its mirror image.

If a racemic mixture of a dissymmetric species is irradiated with circularly polarized light, more light will be absorbed by one enantiomer than by the other. Suppose now that the absorbing species does photochemistry upon irradiation. If a racemic mixture is irradiated with circularly polarized light, one enantiomer will react faster than the other, due to the extinction coefficient difference. This effect can result in asymmetric induction in three different ways. First, the starting material can be enriched in one enantiomer via simple preferential destruction of the other enantiomer (this is known as asymmetric destruction). The second mechanism can operate if the two enantiomers are photochemically interconvertible. In this case, one enantiomer is driven to its mirror image at a rate faster than the back reaction (this is known as partial photoresolution). The third mechanism is possible when the photochemical product is

itself dissymmetric. Here, preferential reaction of one enantiomer can result in optically active products (this is called asymmetric synthesis).

The possibility of using circularly polarized light as a chiral agent was discussed as early as the end of the 19th century by LeBel[5] and van't Hoff[6]. In 1896, Cotton[7] observed circular dichroism in electronic transitions. This made the possibility of chiral induction using circularly polarized light appear even more promising. A number of attempts to observe chiral induction in this manner were reported. It was not until 1929, however, that any of them met with success. In this experiment, Kuhn and Braun[8] observed chiral induction in the CPL photolysis of ethyl-α-bromopropionate.

Since this initial breakthrough, there has been considerable work[9] in the area of chiral induction via photolysis with CPL involving electronic excitation. Induction has been observed[9] via all three previously mentioned mechanisms (asymmetric destruction, partial photoresolution and asymmetric synthesis).

Despite considerable research activity involving optical activity in the UV-visible region and chiral induction employing CPL photolysis via electronic transitions, little was done (until recently) in the infrared. Attempts[10] were made as early as 1954 to observe vibrational circular dichroism (VCD) but (until very recently) none of them met with success. The difficulty was an experimental one. Adequate IR light sources, optics and detection equipment were not available to successfully perform the experiment.

Starting in the late 1960's papers began to appear in the chemical literature discussing the theoretical aspects of vibrational

optical activity. The stated purpose of the early papers was to estimate the magnitudes of the dissymmetry factors g ($g=(\epsilon_R-\epsilon_L)/\epsilon$) for vibrational transitions, and to assess the types of useful molecular information that might be obtained from their experimental measurement. It was hoped that such information would encourage further attempts at the experimental detection of VCD.

In 1968 and 1970, Deutsche and Moscowitz[11,12] published papers dealing with the vibrational optical activity of a helical charged mass distribution, representing an optically active polymer. The predicted g values were in the range 10^{-4} to 10^{-5}. (It should be noted that g values for electronic transitions can be as large as 10^{-2}).

In 1972, Holzwarth and Chabay[13] published a paper employing a model involving two coupled diatomic oscillators. These calculations estimated g values comparable to those calculated by Deutsche and Moscowitz.

VCD was observed in single crystals[14] in 1973. Observed g values were on the order of 5×10^{-4}.

In 1974, the first observation[15] of vibrational circular dichroism in the liquid phase was reported. The vibrational bands in which it was observed were the C*H stretch of 2,2,2-trifluoro-1-phenylethanol ($CF_3CHOHC_6H_5$) $g = 6.5\times10^{-5}$ and the C*D stretch of neopentyl-1-d-chloride ($(CH_3)_3CCHDCl$) $g = 2\times10^{-5}$.

The second observation of VCD in the liquid phase was by Stephens et al[16]. This work was also done with trifluoro-1-phenylethanol. In addition to the C*H stretch, however, VCD was also observed in the OH stretch. The g value reported in this paper for the C*H stretch was

4.3×10^{-5}, that for the OH stretch was 2.5×10^{-5}.

Stephens et al subsequently published two papers in 1976. One work reports[17] the observation of VCD in the combination and overtone bands of camphor, 3-methylcyclohexanone, and β-pinene (1-3μ range). Typical g values ranged as high as 5×10^{-5}. In the other paper[18], VCD of C-H, O-H and N-H stretching bands is reported for a number of molecules. The observed g values range up to 5×10^{-5}.

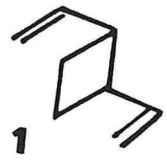
During the past 5 years the field of vibrational optical activity has grown considerably[19]. The early work was restricted to high frequencies for instrumental reasons. Keiderling and coworkers have recently published a series of papers reporting VCD spectra for IR transitions as low as 1300 cm^{-1}.[20] The early observations of g values in the range 10^{-4} - 10^{-5} appear to be typical of VCD spectra in general.

The experimental observation of vibrational circular dichroism makes the possibility of chiral induction via infrared photolysis seem plausible. The fact that pulsed megawatt infrared lasers capable of inducing chemical reactions[21] have become available makes the experiment now possible to perform. This experiment could potentially serve as a probe of the IR chiroptical properties of highly vibrationally excited molecules. The work presented here involves the IR photolysis of a racemic sample of a chiral molecule in the vapor phase using a focused, circularly polarized output from a TEA-CO_2 laser.

RESULTS

The molecule chosen for this study was trans-1,2-divinyl-

cyclobutane (DVB) (**1**). DVB has a number of



characteristics indicating that it may be well suited for this experiment. The thermal chemistry of DVB has been thoroughly studied[22]. The maximum specific rotation[23] is reasonably large $[\alpha]_{365}(CCl_4) = 342^{o}$ and the absolute configuration is known[22]. Pyrolysis[22] of DVB ($E_a \cong 34$ kcal/mole) affords butadiene (**2**), 4-vinylcyclohexene (**3**) and 1,5-cyclooctadiene (**4**).

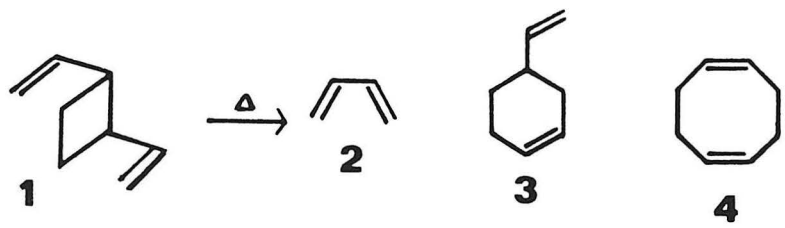


Figure 3

Pyrolysis[23] in the liquid phase (in decane at 146.5°C) gives 4.0% **2**, 70.4% **3** and 25.6% **4**.

Berson and coworkers[22] reported that when optically active trans-1,2-divinylcyclobutane was pyrolyzed (liquid phase in decane at 146.5°C) the resulting 4-vinylcyclohexene showed 8% optical activity (relative to the starting material). Racimization of the starting material occurred only to the extent of 16%. In this pyrolysis 57.7% of the starting material reacted.

It was expected that trans-1,2-divinylcyclobutane could be photolyzed with a pulsed CO_2 laser since the vinyl group should have two vibrational resonances in the tuning range of the laser (9.2 to

10.8 μ).

The gas phase (20 torr) infrared spectrum of trans-1,2-divinylcyclobutane is given in Figure 4.

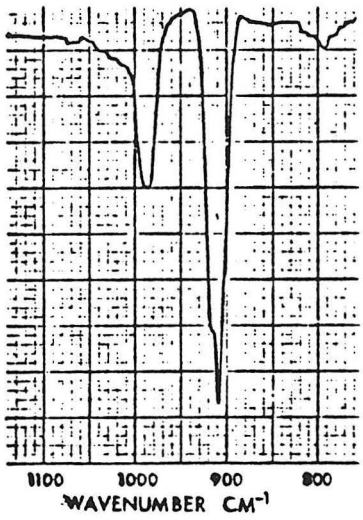


Figure 4. IR spectrum (20 torr gas phase) of trans-1,2-divinylcyclobutane around tuning range of CO_2 laser (923-1086 cm^{-1}).

The peak at 910 cm^{-1} is due[24] to $=CH_2$ out of plane bending and the peak at 990 cm^{-1} is due to =CHR bending. The peak centered at 990 cm^{-1} is more easily accessible with the laser and was used in this study.

The energy output of the laser is dependent on the rotation line used. A number of lines were tried in photolyses of trans-1,2-divinylcyclobutane at their maximum usable energies. The one chosen was the R22 line of the $00^{0}1$-$10^{0}0$ transition (977.2

cm^{-1}=10.23μ). The energy used was 0.8 to 0.9J/pulse.

In choosing the sample pressure at which to carry out the photolysis, one is dealing with two opposing trends. Relatively high pressures will increase the amount of sample processed (necessary for measuring the optical rotation). However, higher pressures will also tend to increase the rate of intermolecular energy transfer due to increased collision rates. Since the success of the experiment depends on preferential absorption by one enantiomer over the other, this intermolecular energy exchange will potentially result in loss of the selectivity. This preferential absorption by one enantiomer over the other is very analogous to isotopic selectivity in multiphoton dissociation. The effect of pressure on the isotopically selective process may therefore provide some idea of the optimum pressure for the present work. Figure 5 shows [25] the effect of pressure on the isotopic selectivity in the CO_2 laser photolysis of SF_6.

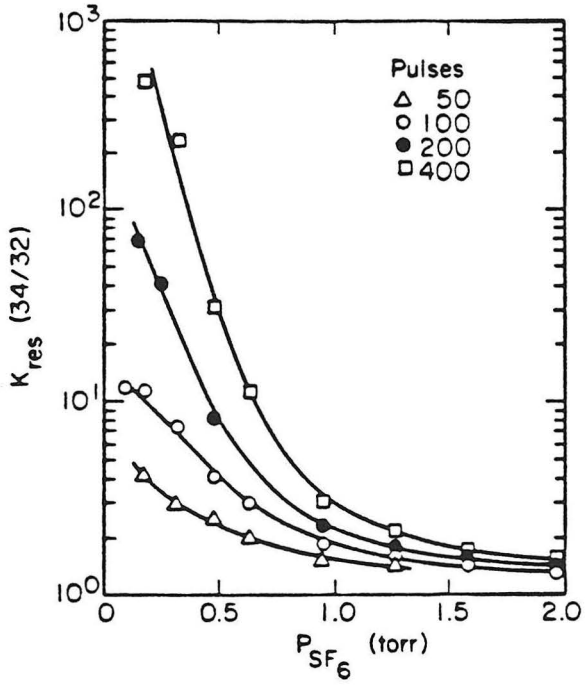


Figure 5. Effect[25] of pressure on the isotopic enrichment in the unreacted SF_6 from the IR laser photolysis of SF_6.

The pressure chosen for this experiment was 0.6 torr, based on Figure 5 and the ease of obtaining this pressure (see experimental section).

The experiment was performed as follows: The laser pulse is already plane polarized when it leaves the laser. The beam was passed through a ZnSe Fresnel prism, giving circularly polarized radiation. This was then focused, using a 15 cm focal length germanium lens, into a gas cell containing 0.6 torr of racemic trans-1,2-divinylcyclobutane. Each sample was photolyzed with 75 pulses (0.8-0.9J/pulse) and the products were then removed by vacuum transfer. A number of individual cell volumes were photolyzed then condensed with decalin and analyzed by VPC (DC-550, 100°C). Product ratios were variable: 1,3-butadiene, 32-38%; trans-1,2-divinylcyclobutane 52-60%; 4-vinylcyclohexene 8-10%, 1,5-cyclooctadiene, 0.7-1.1% (molar ratios). These samples indicate that about 33% of the starting trans-1,2-divinylcyclobutane reacts during the photolysis.

In performing the experiment to check for chiral induction the photolysis procedure was repeated many, many times. The combined sample from these photolyses was separated into its components by preparative VPC (DC-550, 100°C) yielding 44 mg of trans-1,2-divinylcyclobutane and 6 mg of 4-vinylcyclohexene. These were checked for optical activity by means of polarimetry at 365 nm. These samples (in CCl_4) gave observed rotations of $<0.003^{\circ}$. This corresponds to specific rotations of $<0.07^{\circ}$ and $<0.5^{\circ}$ for trans-1,2-divinylcyclobutane and 4-vinylcyclohexene respectively.

Discussion

Though this experiment failed to yield any optical activity it is instructive to determine what magnitude of g value would have been necessary to have observed a measurable rotation in the unreacted DVB. This number can be calculated assuming that no racemization of generated optically active DVB occurs, that only an asymmetric destruction mechanism of chiral induction operates, and that the g value is nonzero only for absorption of the first IR photon. An experimentally observed rotation of 0.01^{o} would have corresponded[26] to a g value of 3.4×10^{-3}. This value is about an order of magnitude larger than the largest values that are observed in VCD spectra. One could hope to obtain an effective g value this large if there was selectivity in absorption of CPL for more than one of the IR photons absorbed by the molecule. At least a dozen photons are absorbed. (The E_a for thermolysis of DVB is 34 kcal/mole and CO_2 laser photons carry only about 3 kcal/Einstein).

In principle, photochemistry with circularly polarized IR laser radiation should give some degree of chiral induction. As mentioned earlier, this experiment is very similar to IR laser isotope separation, an experiment that has been successfully performed in a number of systems[28]. The failure of the experiment described here is probably not a matter of not generating optical activity. It is a matter of not generating enough to measure. To successfully perform the experiment one would like to choose a system with as large a g value as possible. (However, if the g value varies as a function of the degree of vibrational excitation, the $V=0 \longrightarrow V=1$ g value may not

be the determining factor.) The fact that the study of vibrational optical activity is still in its infancy prevents this. To date there has been no report of the observation of VCD in the tuning range of the CO_2 laser. As mentioned earlier, Keiderling and coworkers have been able to measure VCD down to 1300 cm^{-1}.[20] Another possible approach to choosing a molecule with a high g value would be to use a laser near the C-H stretching region[29]. However, even in this region of the IR,knowledge of g values is somewhat limited at this time. When the understanding of vibrational optical activity reaches the point where it is possible to rationally choose a molecule with both a high IR g value and a high UV optical activity (for sensitive detection) this experiment should be repeated.

An alternative approach to this experiment would be to do one photon matrix isolation IR photochemistry[32] on a non-chiral molecule that has chiral rotamers. IR-CPL could be used to drive one conformer to its enantiomer. It has been reported[33] that VCD g values are larger in a matrix than in solution due to decreased cancellation of overlapping transitions with oppositely signed VCD and in limited studies[33] g values approaching 10^{-3} have been observed.

EXPERIMENTAL SECTION

IR photolyses were performed using a Tachisto 215G pulsed CO_2 laser. Energy of the pulses was determined using a Gen. Tec. PRJ-D Joulemeter. The line to which the laser was tuned was determined using an Opt. Eng. CO_2 spectrum analyzer. Pressures were measured using an MKS Instruments type 221 capacitance manometer with a range of 100 torr reading to 0.01 torr.

The plane polarized beam produced by the laser was converted to circularly polarized radiation by sending it through an AR coated ZnSe single pass Fresnel prism (0.6 inch clear aperture) designed for quarter wave retardation in the CO_2 laser wavelength region. The prism was custom made by II-VI Optics, Inc.[34]

The beam was focused into the gas cell using an AR coated germanium meniscus lens (37.4 mm clear aperture) with a focal length of 15 cm (Unique Optical Co.).

Optical rotations were taken in spectral grade carbon tetrachloride using the 365 nm line of a mercury lamp. The measurements were taken on a Perkin-Elmer 141 Polarimeter (readable to 0.001^{o} with an accuracy of $\pm 0.002^{o}$). Samples were held in a 1 dm, 1 mL polarimetry cell. Proton NMR spectra were taken on a Varian Associates A-60 spectrometer. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane in δ units and coupling constants are in Hertz (Hz). Infrared spectra were recorded on a Beckman IR 4210 spectrometer.

Analytical VPC work was done using a Hewlett-Packard 5700A chromatograph (FID) with an HP 3370B electronic integrator. The column used was 10' x 1/8'' 10% DC-550 on 100/120 Chrom P AW-DMCS. Column temperature 100^{o}C. Preparative VPC work was done using a Varian Associates 920 (TC) chromatograph. The column used was 10' x 3/8'' 25% DC-550 on 60/80 Chrom P AW column temperature 100^{o}C.

The gas cell (Figure 6) used in the photolysis is made of glass. It is 13 cm long and 22 mm ID. The ends are fitted with NaCl disk windows (A) sealed at the NaCl-glass interface with Viton o-rings (B). The o-rings have a thin film of Apiezon N vacuum grease on them to

insure a good seal. The salt plates and o-rings are held in place by stainless steel fittings (C) that fit over them and screw onto threaded rings (D) secured to the outside of the cell. There are 2 small fingers (E) coming out of the bottom of the cell, that are sealable via Teflon vacuum valves (F). The cell is filled and emptied via a standard taper joint (G), sealable by a Teflon vacuum valve (F). The o-rings slip around metal rims (H) that keep them from collapsing.

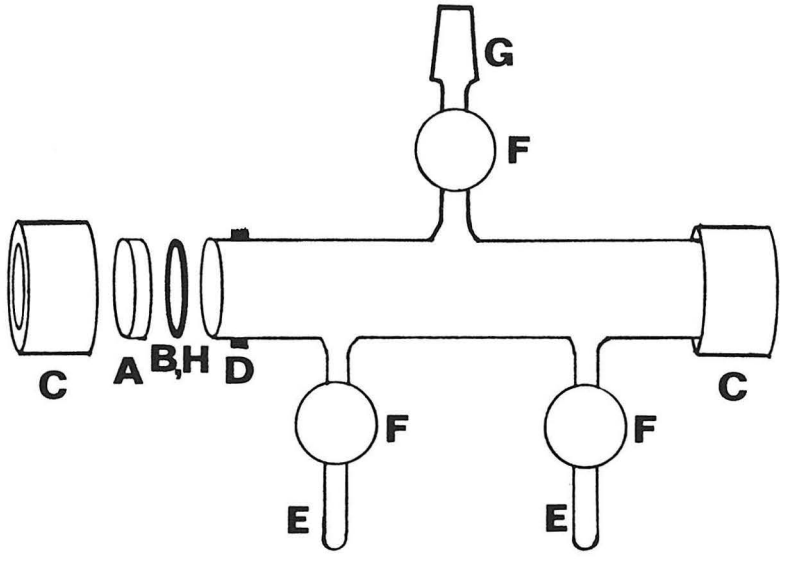


Figure 6. Gas Cell

PHOTOLYSIS PROCEDURE

The experimental set up is shown in Figure 7. The beam (A) leaves the laser (B). The beam enters normal to one face of the Fresnel prism (C). The prism is mounted tilted, so that the edges of the face normal to the beam are at a 45° angle with respect to the plane of polarization of the laser. On leaving the other face of the

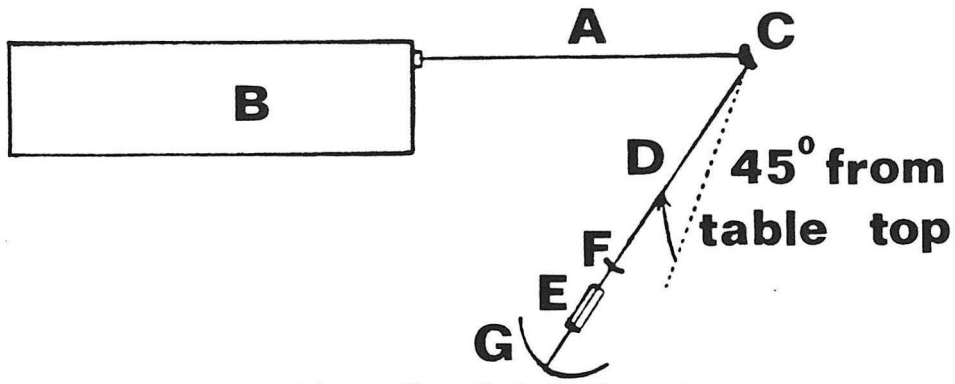


Figure 7. Photolysis set up

prism, the beam (D) is focused into the gas cell (E) by means of the lens (F). The beam terminates at a safety shield used as a beam stop(G).

The material to be photolyzed was placed in one of the cell fingers by vacuum transfer. This finger was then sealed using its valve. This finger was cooled by placing it in a Dewar flask containing an anisole slush[30] (-37°C). This gave a vapor pressure of 0.6 torr. The cell was filled by opening the valve to this finger for 20 seconds. The valve was then closed and the sample was photolyzed with 75 laser pulses (0.8 to 0.9 J each) (1.5 seconds between pulses). Then the valve to the other finger was opened for 15 seconds to collect the photolysis products. This finger was cooled by emersion in a Dewar flask containing liquid nitrogen. This procedure was repeated over and over again until sufficient material was collected. This combined sample was vacuum transferred out of the IR gas cell and separated into its components by preparative VPC. (DC-550, 100°C). The unreacted DVB and the 4-vinylcyclohexene were isolated. Each sample was vacuum transferred out of its VPC collection tube then pipetted into a tared 1 mL volumetric flask. This was weighed and the sample was diluted to 1 mL with spectral grade CCl_4. The samples were

checked for optical activity at 365 nm in a 1 dm, 1 mL polarimetry cell. Each sample gave a rotation of $<0.003^{o}$.

trans-1,2-Divinylcyclobutane (1).

The starting <u>trans</u>-1,2-divinylcyclobutane was prepared by UV photolysis of butadiene in the presence of Michlers ketone as a sensitizer[31]. The material used in the study was purified by preparative VPC. This material was shown to be at least 99.9% pure by analytical VPC (DC-550 $100^{o}C$). NMR (CCl_4) δ 1.55-2.1 (m, 4), 2.45-2.9 (m, 2), 4.7-5.1 (m, 4), 5.55-6.2 (m, 2).

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(26) Let x be the extent of photodestruction.

$$x = 1 - \frac{[R] + [S]}{[Ro] + [S\ o]}$$

[R] and [S] are the amounts of enantiomers remaining after photolysis and [Ro] and [So] represent the initial amounts present. Let y be the enantiomeric excess

$$y = \frac{[R]-[S]}{[R]+[S]} = \frac{[\alpha]\text{observed}}{[\alpha]_{max}}$$

These values are then related[27] by equation (1),

$$(1) \quad x = 1 - \frac{1}{2}\left[\left(\frac{1+y}{1-y}\right)^{1/2-1/g} + \left(\frac{1+y}{1-y}\right)^{-1/2-1/g}\right]$$

This equation was derived[27] for photochemistry resulting from the absorption of one photon. Since vibrational g values are small (on the order of 10^{-4} or less) the exponents in equation (1) will be dominated by the 1/g terms. We can neglect the 1/2 terms giving equation (2) which can be simplified to give equation (5).

$$(2) \quad x = 1 - \frac{1}{2}\left[\left(\frac{1+y}{1-y}\right)^{-1/g} + \left(\frac{1+y}{1-y}\right)^{-1/g}\right]$$

$$(3) \quad (1-x) = \left(\frac{1+y}{1-y}\right)^{-1/g}$$

$$(4) \quad \ln(1-x) = \frac{-1}{g} \ln\left(\frac{1+y}{1-y}\right)$$

$$(5) \quad g = \frac{-\ln\left(\frac{1+y}{1-y}\right)}{\ln(1-x)}$$

An experimentally measured rotation of 0.01^{o} for 44 mg of DVB would correspond to a specific rotation of 0.23^{o}. This gives a value for y of 6.7×10^{-4}. The value of x was experimentally determined to be 0.33. The value for g corresponding to these parameters determined using equation (5) is 3.35×10^{-3}.

Calculating x using this g value and $y=6.7x10^{-4}$ in equation (1) gives a value for x of 0.33 indicating that the simplified equation (5) is adequate for this case.

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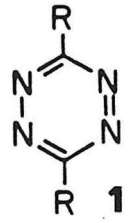
Chapter 3

On the Intermediacy of Triazolenitrenes in the Photodecomposition of s-Tetrazine.

Chapter 3

1,2,4,5-Tetrazine (s-tetrazine) and its substituted derivatives (**1**) have been of interest to spectroscopists and photochemists for some time. The spectroscopy and photophysics of these substances have been investigated by a number of workers.[1,2,3,5,7,10,20]



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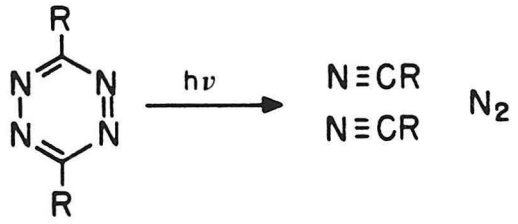
s-Tetrazine is known to have two transitions[4] in the range 500-700 nm. These correspond to excitation into $^1B_{3u}$ and $^3B_{3u}$ states and both are $n \longrightarrow \pi^*$ in nature. The parent molecule in known[4] to photodissociate into molecular nitrogen and HCN following excitation into either of these electronic states. (scheme 1, R=H)

Scheme 1



The first clear indication that s-tetrazine photochemistry is more complicated than scheme 1 indicates was the report by Burland and coworkers[9,13] that in mixed crystals at 2°K the photodissociation (S_1 origin) of both the parent molecule (ST) (in benzene) and the 3,6-dimethyl derivative (DMST) (in p-xylene or durene) depends

quadratically on the intensity of the light. This dependence was also observed for DMST for a laser line with vibronic energy. It was concluded from these observations that the photodissociation under these conditions requires the absorption of two photons. To help determine[13] whether the state reached by the 2 photon process is the same as would be reached by one photon of twice the energy,the dye laser output was doubled to 290 nm. If the same state is reached, the 290 nm intensity dependence should be linear. The experimentally observed result for s-tetrazine (ST) in benzene was a quadratic dependence. These workers then did an experiment with two light sources. The first source (a filtered tungsten lamp) was of correct wavelength to excite the ST molecule into its S_1 state. The second light source was a dye laser tuned (586 or 574 nm) so it would not be absorbed by an ST molecule in its ground state. Neither the lamp nor the laser by itself resulted in measurable photodecomposition but together gave rise to photodissociation. When the dependence on the intensity of these sources was measured, instead of the expected linear dependence on each source a quadratic dependence on both the lamp and laser intensity was observed!

s-Tetrazines do not exhibit quadratic intensity dependence under all circumstances.[3,9,10,11,13,14,15,16,19] For example, Karl and Innes[3] had previously indicated a linear intensity dependence (552 nm, S_1) for the parent system in the gas phase and Burland and coworkers[13] found a linear intensity dependence for the photolysis of ST in hexane at room temperature (254 nm, S_2 and 535 nm, S_1). Hochstrasser and coworkers[11] found that for matrix isolated ST at 4.2°K the intensity dependence was linear under broad band illumination but quadratic when

only the origin region (0-0band) was excited. They also found[11] that photolysis of DMST and phenyl-s-tetrazine in solution at room temperature displays a quadratic intensity dependence.

In 1978 Hochstrasser and coworkers[11] reported that pulsed (337 nm, S_2) excitation of DMST, phenyl-s-tetrazine and diphenyl-s-tetrazine in solution (EtOH) caused the generation of transients that absorb in the visible (600-700 nm). The transient signal strength depended linearly on the intensity of the light source. These transients were believed to be intermediates generated by the absorption of one photon. It was proposed that the intermediates could either go back to s-tetrazine or absorb a second photon and go on to nitrile products and molecule nitrogen: thus the quadratic intensity dependence. A similar absorption was reported in 1979 by Burland and coworkers[14,15] in the 588 nm pulsed irradiation of DMST in durene at 2^{o} K. In the situations where the intensity dependence is linear, presumably either the intermediate does not need a second photon to decompose or the excited s-tetrazine goes directly to nitrile and molecular nitrogen, bypassing the intermediate.

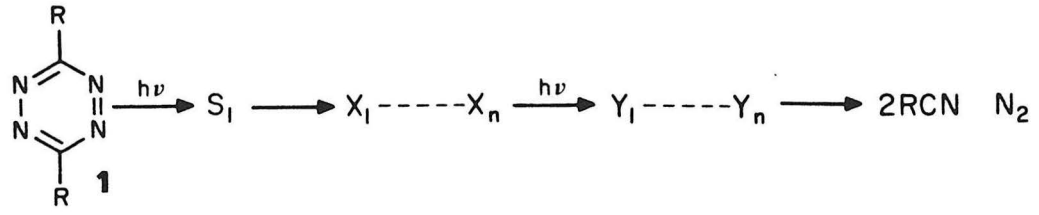
In 1980 Hochstrasser and coworkers[18] reported additional work on the transients that they had observed and concluded that they are not generated in sufficient amounts to be involved in the principal photochemical pathway.[21] Burland and coworkers[16,19] have also concluded that the transient absorption that they observed was not the species responsible for absorption of the second photon. Using a new holographic technique these workers investigated the photochemical action spectrum for DMST in poly(vinylcarbazole) at room temperature and concluded that there is a species responsible for the absorption

of the second photon but that it has an absorption spectrum similar to the DMST $S_0 \rightarrow S_1$ transition (about 540 nm). From the constraints of hologram formation, their CW laser intensity and the known photophysical behavior of s-tetrazines Burland and coworkers concluded that the transient that absorbs the second photon is probably not an excited state of the starting DMST but rather some distinct metastable chemical species.

In another study of the mechanism of s-tetrazine photochemistry, Hochstrasser[6] and coworkers prepared the labeled species s-tetrazine-1,4 $^{15}N_2$. This was photolyzed in the gas and solid phases at room temperature by excitation into S_1, T_1 or S_2. In all cases the N_2 that was formed in the photolysis was $^{14}N\ ^{15}N$. These workers concluded that for these conditions 1,4 nitrogen-nitrogen bonding plays a negligible role in the overall photochemical decomposition. Studies have also been done on the vibrational[12] and translational[17] energy content of the fragments from the gas phase photodecomposition of s-tetrazine. In addition ST has been successfully used in photochemical isotope separation studies[3,4,5,7] and its triplet spin substates have been shown to exhibit different photochemical reactivities.[8]

In summary, the photochemistry of s-tetrazines is believed to involve the absorption of a photon followed by rearrangement to one or more distinct chemical species (scheme 2). The system reaches a species that under some circumstances requires absorption of a second photon to continue on to nitrile products and molecular nitrogen. The nature and number of chemical species involved are unknown.

Scheme 2



Whether or not there are any species (Y) that are metastable after the absorption of the second photon is unknown.

The generation of triazolenitrenes (2) by the oxidation[23,24,25,26] (0 or 25°C) of the corresponding aminotriazoles (scheme 3) has been shown to produce nitriles and molecular nitrogen.

Scheme 3

Triazolenitrenes (2) are isomers of the corresponding substituted s-tetrazines (1). It seems plausible in light of these facts that triazolenitrenes could be involved in the photochemistry of s-tetrazines[27].

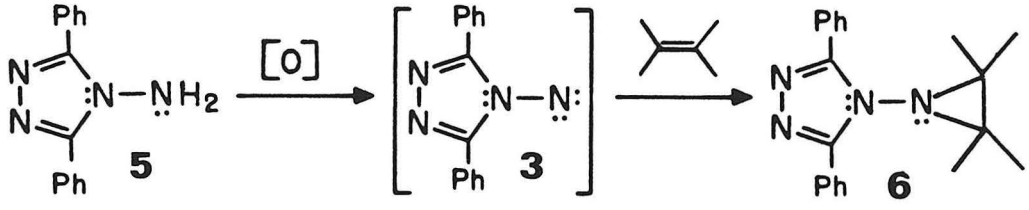
To explore the possibility that triazolenitrenes are involved in the photochemical decomposition of s-tetrazines, conditions were found where a substituted triazolenitrene was efficiently trapped to give a

stable product when generated (scheme 3) oxidatively. The correspondingly substituted s-tetrazine was then photolyzed under these conditions and a search was made for the trapped triazolenitrene product. An attempt was also made to prepare a kinetically persistent triazolenitrene at low temperatures to directly characterize the spectral properties and examine the thermal and photochemical behavior of such a species to address the question of its possible involvement in s-tetrazine photochemistry. These efforts are described below.

Results: Trapping Studies

The system chosen for the trapping study was (2,5-diphenyl-1,3,4 triazolidyl)nitrene (**3**) and 3,6-diphenyl-1,2,4,5 tetrazine (**4**) in solvent mixtures containing methanol.[28] It was found that oxidation[25,26] (lead tetraacetate) of 1-amino-2,5-diphenyl-1,3,4 triazole (**5**) in a 50/50 methanol/tetramethylethylene mixture (this is about 4.2 molar in olefin) resulted in the production of a high yield (78%) of the adduct (**6**), presumably from the reaction of transient nitrene **3** and alkene.

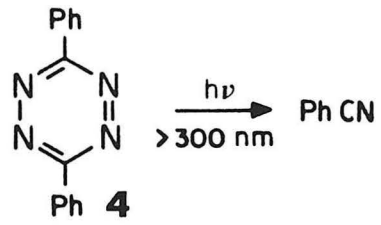
Scheme 4



It was also found that room temperature photolysis of (**4**) (6.6 millimolar in 50/50: methanol/THF, λ>300 nm) for 5 hours yielded a

4.6% conversion to benzonitrile (by UV), and no (<5% by NMR) new nonvolatile products.[21,22]

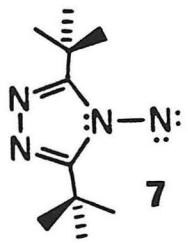
Scheme 5



Photolysis of (**4**) under the trapping conditions (6.6 millimolar in 50/50 methanol/tetramethylethylene, λ>300 nm) for 5 hours yielded[29] less than 0.01% of (**6**) (by HPLC). The adduct (**6**) was shown to be photostable[30] under these photolysis conditions.

Results: Attempted Preparation of a Persistent Triazolenitrene.

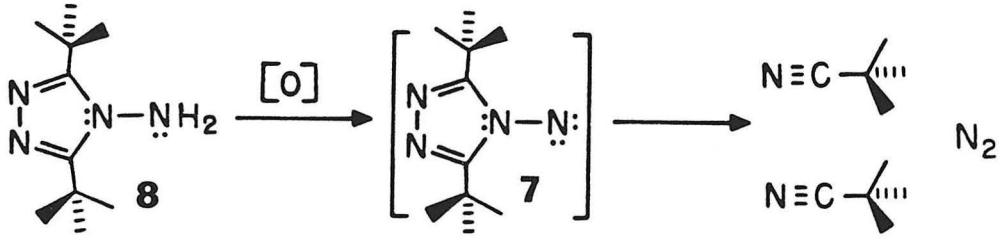
The molecule chosen as the target for this study was (2,5-di-tert-butyl-1,3,4-triazolidyl)nitrene (**7**).



The tert-butyl groups were incorporated into the structure to slow[38] the dimerization reaction to the corresponding tetrazene. The strategy used was to attempt the generation of this compound by oxidation of 1-amino-2,5-di-tert-butyl-1,3,4 triazole (**8**) and detect

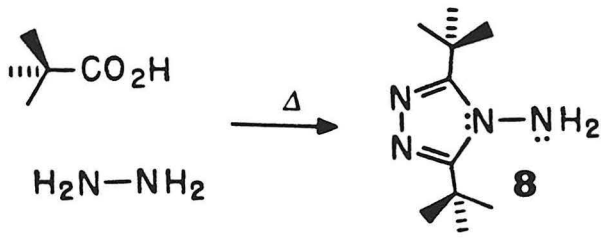
the formation of (7) by looking for color.[39,40] Low temperatures were used in an attempt to minimize the unimolecular decomposition pathway yielding trimethylacetonitrile and molecular nitrogen (scheme 6).

Scheme 6



The synthetic route that was devised to prepare (8) was the sealed tube pyrolysis of a mixture of trimethylacetic acid and hydrazine (scheme 7).

Scheme 7



A tetrahydrofuran (THF) solution of (8) plus 1.25 equivalents of triethylamine at -78°C was treated with 1.0 equivalent of tert-butyl hypochlorite in the dark. After stirring for 2.5 hours at -78°C the mixture was filtered(-78°C) through basic alumina (to destroy[41] any remaining oxidant) and the filter was washed with prechilled THF. This reaction resulted in 18% of the starting (8) being converted to

trimethylacetonitrile and 81% being recovered unreacted. No color was observed in the reaction mixture at any time. These observations indicate[42] that species (**7**) is formed but is not stable to unimolecular decomposition at -78°C. Attempts were therefore made to oxidize (**8**) at lower temperatures. The conditions that were tried are listed in Table 1. No colors developed in any of the reaction mixtures (with the exception of the last entry).

Table 1: Very Low Temperature Attempts to Oxidize (8).

Reagents[a]/solvent[a]		temperature	time
TBHCl TEA DME	1 equiv. 1.25 equiv.	-116°C	1.75h
TBHCl TEA DME	5 equiv. 6.25 equiv.	-116°C	1.5h
TBHCl TEA DME	1 equiv. 1.25 equiv.	-127°C	1.5h
TBHCl TEA DME	5 equiv. 6.25 equiv.	-127°C	1.3h
TBHBr TEA DME	1 equiv. 1.25 equiv.	-116°C	1 h
TBHBr TEA DME	5 equiv. 6.25 equiv.	-116°C	1.5h
TBHBr TEA DME	1 equiv. 1.25 equiv.	-127°C	1.5h
TBHBr TEA DME	5 equiv. 6.25 equiv.	-127°C	1.5h
ozone[b] TEA DME	 1.25 equiv.	-116°C	

(a) TBHCl = tert-butyl hypochlorite, TEA = triethylamine, TBHBr = tert-butyl-hypobromite, DME = Dimethyl ether.

(b) As more ozone was bubbled in at intervals the reaction mixture eventually acquired the blue color of ozone.

Experimental Section

Melting points were determined by using a Thomas-Hoover melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 257 infrared spectrophotometer. Proton NMR spectra were obtained on a Varian Associates EM-390 spectrometer. Chemical shifts are reported as parts per million (ppm) downfield from tetramethylsilane in δ units and coupling constants are in Hertz (Hz). NMR data are reported in this order: chemical shift, multiplicity, s=singlet, d=doublet, t=triplet, m=multiplet; number of protons; coupling constants. Packed column analytical VPC was done using a Hewlett-Packard 5700A gas chromatograph equipped with a flame ionization detector and nitrogen carrier gas. This instrument was used with 0.125 inch packed stainless steel columns. All quantitative VPC analysis was accomplished using a Hewlett-Packard 3370B electronic integrator. Corrections were made for detector response. For preparative VPC a Varian Associates 920 instrument equipped with a thermal conductivity detector and helium carrier gas was used. This instrument was used with 0.375 inch aluminum packed columns. Visible and UV spectra were recorded using a Beckman model 25 spectrophotometer. HPLC work was done using a Waters analytical instrument equipped with a UV detector (254 nm) and a 1 ftxl/4 inch microporasil column. The solvent system used for all work was 3/1 ethyl acetate/hexane. Ozone was obtained from a Welsbach ozone generator.

For photolyses spectral grade methanol was used and tetramethylethylene (Fluka $\geq$ 98%) was purified by preparative VPC (10 ft 25% DC-550 on 60/80 Chrom P-AW, 80^{o}C). Lead tetraacetate (LTA) was

recrystallized from acetic acid. Ethyl acetate used as an HPLC solvent was distilled under an inert atmosphere. Tetrahydrofuran (THF) was distilled from benzophenone/sodium under an inert atmosphere. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

4-Amino-3,5-Diphenyl-1,2,4-Triazole (5). This compound was prepared by the acid rearrangement of 3,6-diphenyl-1,2-dihydro-1,2,4,5 tetrazine as described in the literature.[31] M.P. 265-266°C lit. [32] M.P. 268-269°C. NMR (DMSO-d_6) δ 7.9-8.2 (m, 4), 7.4-7.7 (m, 6), 6.3 (s, 2).

3,6-Diphenyl-1,2-Dihydro-1,2,4,5-Tetrazine. This compound was prepared from hydrazine and benzonitrile as described by Abdel-Rahman, Kira and Tolba.[33] M.P. 190.5-192°C, lit.[33] M.P. 192-193°C. NMR (DMSO-d_6) δ 9.1 (s, 2), 7.7-7.9 (m, 4), 7.3-7.5 (m, 6).

3,6-Diphenyl-1,2,4,5-Tetrazine (4). This compound was prepared from 3,6-diphenyl-1,2-dihydro-1,2,4,5-tetrazine using the procedure of Huisgen, Sauer and Seidel.[34] The product was recrystallized (ethyl acetate) then chromatographed (silica gel/dichloromethane). The beautiful purple crystals had an M.P. of 196-196.5°C lit.[34] M.P. 193-195°C. NMR ($CDCl_3$) δ 8.55-8.8 (m, 4), 7.5-7.75 (m, 6). UV (methanol) 296 nm (ϵ 36,200), 218 (ϵ 9600).

Trapping Product (6). A 25 mL round bottom flask was charged with 0.20 g (0.85 mmole) of 4-amino-3,5-diphenyl-1,2,4-triazole (5), 3 mL methanol, 3 mL tetramethylethylene and a magnetic stir bar. The solution was cooled to 0°C and degassed by bubbling a stream of nitrogen through it for 20 minutes. The solution was warmed to room temperature and 0.38 g (0.86 mmole) of lead tetraacetate (LTA) was

added over 70 minutes with stirring by means of a solid addition tube. Stirring was continued for 35 minutes at room temperature. The mixture was combined with 40 mL dichloromethane then washed with 3x8 mL of satd. sodium chloride solution. The organic phase was dried (Na_2SO_4) and the solvent removed yielding 0.21 g (78%) of white product. This was recrystallized from ethanol/water. (It is crucial to remove all acetic acid before this recrystallization or the product will decompose) M.P. 253-254.5°C (decomp.), NMR ($CDCl_3$) δ 7.8-8.05 (m, 4), 7.4-7.6 (m, 6), 1.2 (s, 6), 0.5 (s, 6), Anal. Calcd. for $C_{20}H_{22}N_4$: C, 75.44; H, 6.96; N, 17.59. Found: C, 75.49; H, 7.06; N, 17.58. UV (methanol) 257 nm (ϵ20,600).

4-Amino-3,5-Di-tert-butyl-1,2,4-Triazole (8). 30 mL thick walled glass tubes were charged with 7.1 g (70 mmole) of trimethylacetic acid and 2.2 g (70 mmole) of hydrazine.[36] The tubes were then degassed on a vacuum line and sealed under vacuum. They were then gradually heated to 220°C over a 24 hour period then held at this temperature for 3 days. (Caution should be exercised. These tubes would often explode and hydrazine is extremely toxic and a suspected carcinogen). The tubes were then allowed to cool to room temperature. They were then frozen (liquid nitrogen) and broken open. The reaction mixture was then heated to 210°C in an open flask in a good fume hood. About 75 g of the reaction mixture was heated with 15% aqueous sodium hydroxide for about 20 hours (oil bath 120°C) under an inert atmosphere. The resulting mixture was then extracted with dichloromethane and this organic phase washed with saturated aqueous sodium chloride. The solvent was removed at reduced pressure and the resulting solid (19g) was heated with 15% aqueous sodium hydroxide for

12 hours (oil bath 120°C). The material was again refluxed with 15% aqueous sodium hydroxide then filtered hot. The collected solid was washed with 15% aqueous sodium hydroxide then water. The solid was then taken up in dichloromethane, washed twice with saturated aqueous sodium chloride, dried and the solvent removed at reduced pressure yielding 4.1 g of product. An additional 5.2 g was recovered by saturating the water wash liquid with sodium chloride then extracting the resulting solid into dichloromethane, washing this twice with saturated aqueous sodium chloride, drying the organic solution (Na_2SO_4) then removing the solvent at reduced pressure. The product was sublimed. (150°C, 0.3 torr) M.P. 210.5-211°C; IR (Nujol Mull) 3365, 3230, 1645 (weak), 1520, 1300, 1215, 1000, 885. NMR ($CDCl_3$)δ 4.6 (s, 2), 1.5 (s, 18). Anal. Calcd. for $C_{10}H_{20}N_4$: C, 61.19; H, 10.27; N, 28.54. Found: C, 61.35; H, 10.40; N, 28.76.

Photolysis Procedure

Samples were contained in 5 mm ID quartz tubes. They were degassed prior to photolysis by cooling the tube to 0°C then bubbling a slow stream of N_2 through the solution for about 15 minutes. The samples were then warmed to room temperature and any precipitated material redissolved. The photolyses were performed with a Hanovia medium pressure mercury lamp filtered by a 1 mm thick Schott WG-335 filter (λ>300 nm). Samples were held in a quartz dewar of water. Benzonitrile was measured by taking the UV spectrum of the vacuum transferred solvent. Samples were prepared for HPLC analysis by removing solvents under vacuum, dissolving the residue in dichloromethane, filtering through a Millipore assembly, removing the

dichloromethane, adding the desired solvent, sealing in an ampoule then storing in liquid nitrogen until ready for analysis.

Oxidation of (8) at -78°C with Basic Alumina Filtration.

A round bottom flask was charged with 50 mg (0.26 mmole) of (8), 10 mL of THF and a magnetic stir bar. The stirred solution was cooled to -78°C and 44 μL (0.319 mmole) of triethylamine was added. With continued stirring at -78°C, 30.4 μL (0.26 mmole) of tert-butyl hypochlorite was added slowly by syringe. After continued stirring at -78°C for 2.5 h the mixture was transferred via Teflon tubing to a short column at-78°C packed with 1 inch of basic alumina. The solution was pulled onto the basic alumina then 30 mL of THF (prechilled to -78°C) was added via Teflon tubing to this short column and pulled through into the receiver at -78°C. The resulting solution was warmed to room temperature and after vacuum transfer the volatiles were analyzed for trimethylacetonitrile by VPC. (9N9/KOH on 100/120 Chrom P, temperature programmed at 70°C for 18 minutes then up to 100°C at a rate of 32°/minute). Using cyclooctane as internal standard this analysis revealed that 18% of the starting (8) had been converted to trimethylacetonitrile. The identity of the trimethylacetonitrile was verified by coinjection. After warming the basic alumina column to room temperature it was washed with 60 mL of 3/1 dichloromethane/methanol. This was evaporated and the residue isolated. The residue from the THF wash was also isolated. These were checked by NMR and the total recovered unreacted (8) was 81% ($CHCl_3$ as standard). To verify that the column of basic alumina destroys tert-butyl hypochlorite at -78°C a flask was charged with 10

mL THF and cooled to -78°C. Then 44.4 μL of triethylamine was added with stirring. This was followed by the slow addition of 30.4 μL of tert-butyl hypochlorite. This solution was stirred at -78°C for 2 h. It was then transferred to a 1 inch column of basic alumina at -78°C and washed down with 30 mL of pre-chilled (-78°C) THF as before. The receiver contained 50 mg of (8) and 44 μL triethylamine at -78°C. The resulting mixture was stirred at -78°C for 2.5 h. After warming to room temperature the volatiles were vacuum transferred away and found to contain $\leq$0.5% trimethylacetonitrile.

Very Low Temperature Attempts at Oxidation of (8).

In a typical run a round bottom flask was charged with 50 mg of (8) and the appropriate amount of triethylamine. The flask was cooled to -78°C and about 10 mL of dimethyl ether was condensed into the flask. The mixture was stirred for a while then cooled to the desired temperature with either an LN_2/ethanol slush (-116°C) or LN_2/n-propanol (-127°C). The desired oxidant was then added slowly. Note that at these extremely low temperatures the solubility of (8) is low. Much of the solid was not in solution.

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(27) The observation[24] that dimethyltriazolenitrene (2), R=CH_3) (generated by the oxidation of the corresponding N-amino) decomposes in solution at room temperature to give a high yield of acetonitrile coupled with the report by Hochstrasser[11] and coworkers that the photodecomposition of DMST exhibits a quadratic dependence on light intensity in solution at room temperature argues against (2) being the species that requires the absorption of the second photon to decompose to nitrile products (or any X species in scheme 2).

(28) This work was done after Hochstrasser and coworkers[11] had observed a transient absorption for the flash photolysis of diphenyl-s-tetrazine but prior to their report[18] that this transient is not the species that absorbs the second photon. An attempt was made to match these workers conditions fairly closely. The diphenyl system was used in an alcohol solvent at room temperature and the photolysis employed U.V. radiation.

(29) TLC of the photolysis mixture reveals the formation of at least 2 major unidentified photoproducts. For TLC on silica gel (3/1 ethyl acetate/hexane)diphenyl-s-tetrazine (4) has an Rf of 0.69, the unknown products have Rf values of 0.61 and 0.53 while (6) has an Rf of 0.08. These same conditions were used for the HPLC work and these 3 fast moving compounds

came off as 1 peak with the heavy loadings used and were recovered. NMR analysis of the residue after removal of solvent showed about 60% unreacted (4) and 40% unidentified new compounds. (Based on the aromatic region). These new multiplets were ($CDCl_3$) δ 7.8-8.1 ppm, area 3; 7.2-7.5 ppm, area 25; 0.8-2.0 ppm, area 48.

(30) A solution of (6)(0.24 mmolar) and (4) (6.6 mmolar) in 50/50 methanol/tetramethylethylene was photolyzed (λ >300 nm) for 5 hours. HPLC analysis of this mixture showed no detectable loss of (6).

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(40) 1,1-Dialkyl-diazenes are colored compounds[39] and it would not be unreasonable to expect species (7) to also be colored.

(41) A comparable solution of triethylamine and tert-butyl-hypochlorite (with no (8)) in THF at -78°C was filtered through basic alumina (-78°C) and the filter washed with prechilled THF. The receiver of the filtered solution (at -78°C) contained a sample of (8) plus additional triethylamine. After the filtration this receiver was stirred for 2.5 h at -78°C. This resulted in $\leq$0.5% conversion to trimethylacetonitrile.

(42) Alternatively species (7) is not a colored molecule. The concentration of (7) that would have been present if the species was stable should have been within a factor of 3 or 4 of the intensely purple solutions of (2,2,6,6-tetramethylpiperidyl)nitrene observed by Hinsberg.[35]